Supporting information

Regenerative glycosylation under nucleophilic catalysis

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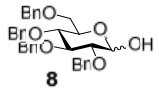
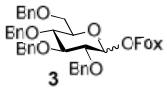
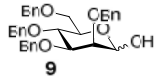
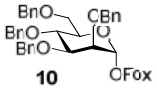
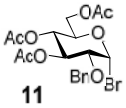
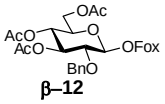
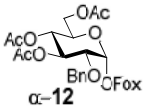
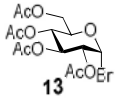
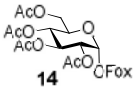
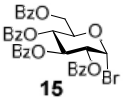
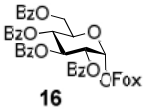
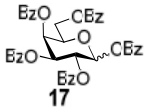
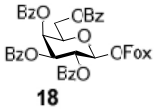
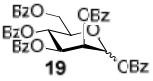
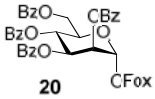
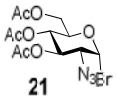
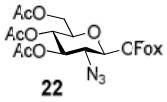
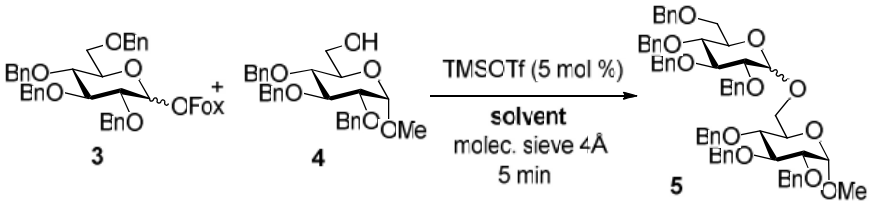
Contents

Table 1S. Synthesis of 3,3-difluoro-3*H*-indol-2-yl (OFox) imidates

Entry	*Starting material*	*Conditions,*[a] *temp, time*	*Product*	*Yield, α/β ratio*
1	 **8**	**A**, rt, 8 h	 **3**	62% 10/1
2	 **9**	**A**, rt, 12 h	 **10**	61% α only
3	 **11**	**B**, 0 °C, 40 min	 **β–12**	80% β only
4	**11**	**B**, rt, 5 h	 **α–12**	81% α only
5	 **13**	**C**, rt, 6 h	 **14**	80% α only
6	 **15**	**B**, rt, 10 h	 **16**	75% α only
7	 **17**	**D**, 0 °C to rt, 6 h	 **18**	75% β only
8	 **19**	**D**, rt, 2.5 h	 **20**	84% α only
9	 **21**	**B**, 0 °C to rt, 3 h	 **22**	70% β only

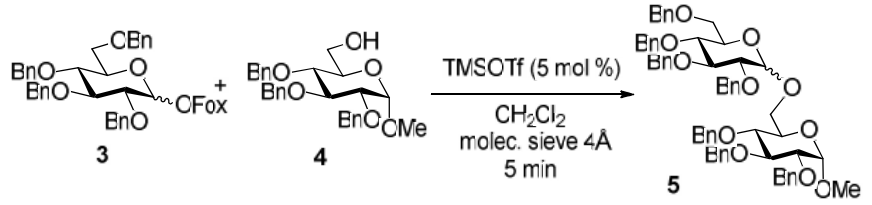
[a] – Conditions:
A: i) $SOCl_2$, DMF, CH_2Cl_2, ii) 3,3-difluoroxindole, Ag_2O, DIPEA, CH_2Cl_2;
B: 3,3-difluoroxindole, Ag_2O, DIPEA, CH_2Cl_2;
C: 3,3-difluoroxindole, Ag_2O, DIPEA, toluene;
D: i) 33% HBr/AcOH, CH_2Cl_2, ii) 3,3-difluoroxindole, Ag_2O, DIPEA, CH_2Cl_2

Table 2S. The effect of solvents on the stereoselectivity of glycosidation of per-benzylated OFox donor **3**.



Entry	*Solvent*	*Temp*	*Yield of **5**, %*	*α/β ratio*
1	CH_2Cl_2	-78 ^oC	94	1/24
2	Et_2O	-78 ^oC	84	1/5.0
3	Et_2O	50 ^oC	81	1.6/1
4	THF	50 ^oC	79	1.4/1
5	CH_3CN	-40 ^oC	87	1/14
6	EtCN	-78 ^oC	99	β only
7	CH_2Cl_2/CH_3CN (1/2, v/v)	-40 ^oC	96	1/6.0
8	CH_2Cl_2/CH_3CN/EtCN (1/2/1, v/v/v)	-78 ^oC	99	β only

Table 3S. Temperature dependence on the stereoselectivity of glycosidation of per-benzylated OFox donor **3**.

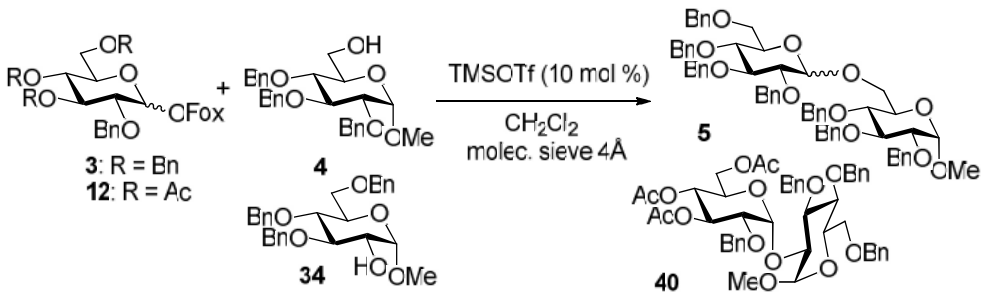


Entry	*Temp*	*Yield of **5**, %*	*α/β ratio*
1	-78 ^oC	94	1/24
3	-40 ^oC	97	1/8.0
4	rt	93	1/1.2
5	50 ^oC	93	1/1.0

Table 4S. The effect of dilution on the stereoselectivity of glycosidation of per-benzylated OFox donor **3** with acceptor **4** in the presence of TMSOTf.

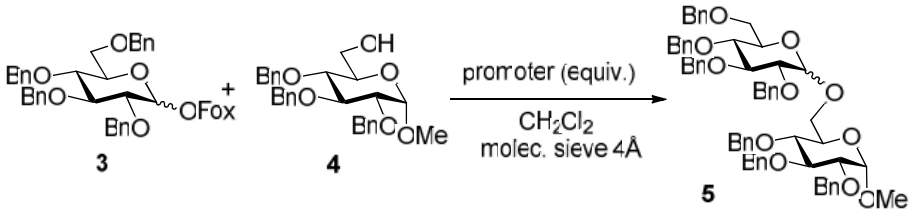
Entry	*Solvent*	*Temp, time*	*Yield of **5**, %*	*α/β ratio*
1	CH_2Cl_2 (86 mM)	-78 ^oC, 10 min	94	1/24
2	EtCN (86 mM)	-78 ^oC, 10 min	99	β only
3	CH_2Cl_2 (17 mM)	-78 ^oC, 10 min	88	1/24
4	EtCN (17 mM)	-78 ^oC, 10 min	97	β only

Table 5S. The effect of anomeric configuration on the stereoselectivity of glycosidation of OFox donors **3** and **12**



Entry	*Donor*	*Acceptor*	*Temp., time*	*Product, yield, %*	*α/β ratio*
1	**3** (α/β = 10/1)	**4**	-78 °C, 5 min	**5**, 94	1/24
2	α-**3**	**4**	-78 °C, 5 min	**5**, 98	1/24
3	α-**12**	**34**	rt, 15 min	**40**, 88	α only
4	β-**12**	**34**	rt, 15 min	**40**, 89	α only

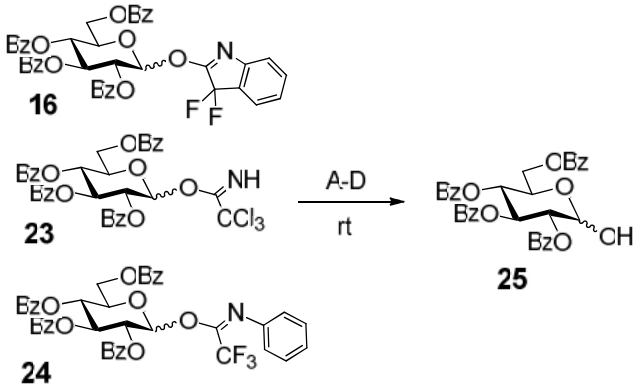
Table 6S. The effect of promoter on the stereoselectivity of glycosidation of per-benzylated OFox donor **3**



Entry	*Promoter (equiv.)*	*Temp, time*	*Yield of **5**, %*	*α/β ratio*
1	TMSOTf (0.05 equiv.)	-78 °C, 5 min	94	1/24
2	TMSOTf (0.05 equiv.)[a]	-78 °C, 10 min	84	1/5.0
3	BF_3-OEt_2 (0.1 equiv.)	-78 °C, 5 min	93	1/20
4	$Cu(OTf)_2$ (0.2 equiv.)	-78 °C, 5 min	97	β only
5	MeOTf (0.2 equiv.)	-78 °C, 10 min	91	>1/25
6	AgOTf (0.5 equiv.)	rt, 24 h	71	1/1.6
7	$PdCl_2$ (0.3 equiv.)	rt, 36 h	57	1/1.7
8	$TMSClO_4$ (0.1 equiv.)[a]	rt, 10 min	75	5.0/1
9	$TMSClO_4$ (0.1 equiv.)[b]	rt, 5 min	54	6.2/1
10	$Bi(OTf)_3$ (0.1 equiv.)	-78 °C, 5 min	85	1/7

[a] - Et_2O was used as the reaction solvent;
[b] - A mixture of Et_2O/1,4-dioxane (1/1, v/v) was used as the reaction solvent

Table 7S. Comparative hydrolytic stability study of OFox, trichloro- and trifluoroacetimidates under various reaction conditions



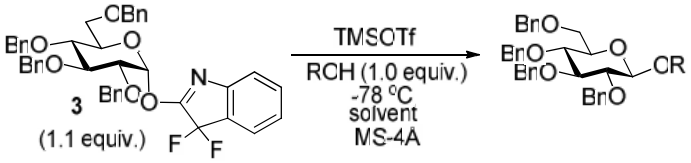
For these studies, per-benzoylated OFox glycosyl donor **16** was compared with 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate **23** and 2,3,4,6-tetra-*O*-benzoyl-α,β-D-glucopyranosyl *N*-phenyltrifluoroacetimidate **24.** These studies were performed in the presence of various Lewis acids in wet $ClCH_2CH_2Cl$. A mixture of imidate (**16**, **23**, or **24**, 0.01 mmol), promoter (A-D, see below, 0.013 mmol) in $ClCH_2CH_2Cl/H_2O$ (0.5 mL, 500/1, v/v) was stirred for 24 h at rt. Quantitative estimates were made at 1, 16 and 24 h time points and are based on the accumulation of 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose **25**,[1] as observed by TLC (R_f = 0.45, ethyl acetate/hexanes, 3/7, v/v).

Entry	*Donor*	*Conditions*[a]	*% of hemiacetal **25** formed after*		
			1 h	*16 h*	*24 h*
1	**16**	A	quant.	quant.	quant.
2	**23**	A	50	60	60
3	**24**	A	40	50	50
4	**16**	B	0	0	0
5	**23**	B	0	0	0
6	**24**	B	0	0	0
7	**16**	C	0	quant.	quant.
8	**23**	C	0	0	20
9	**24**	C	0	0	0
10	**16**	D	0	0	50
11	**23**	D	0	10	quant.
12	**24**	D	0	70	quant.

[a] Conditions:

A: BF_3-OEt_2 (0.1 equiv.);
B: $Bi(OTf)_3$ (0.1equiv.);
C: MeOTf (1.0 equiv.);
D: $PdCl_2$ (0.1 equiv.)

Table 8S. TMSOTf-promoted glycosidation of OFox donor **3** with different acceptors in CH_2Cl_2 or EtCN at -78 ^oC



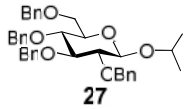
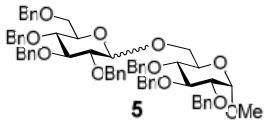
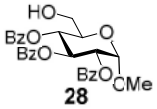
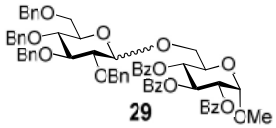
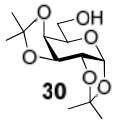
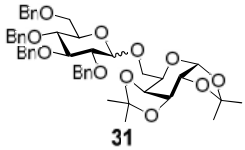
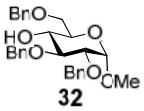
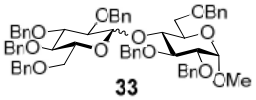
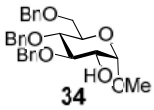
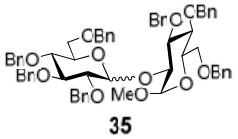
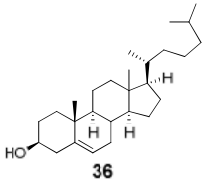
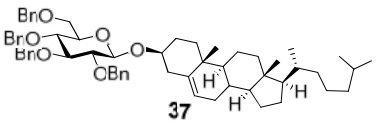
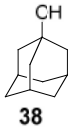
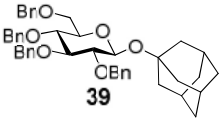
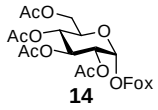
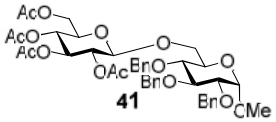
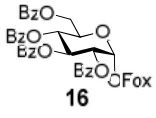
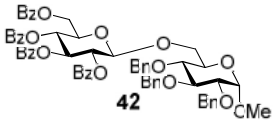
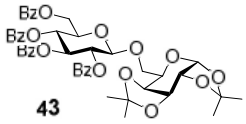
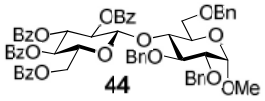
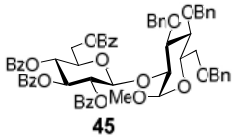
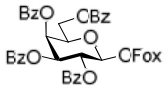
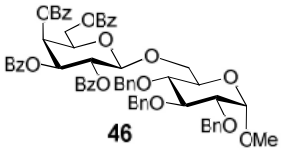
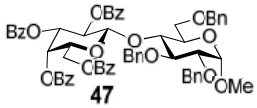
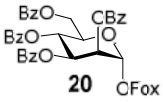
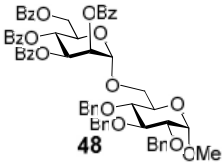
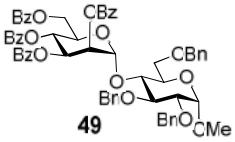
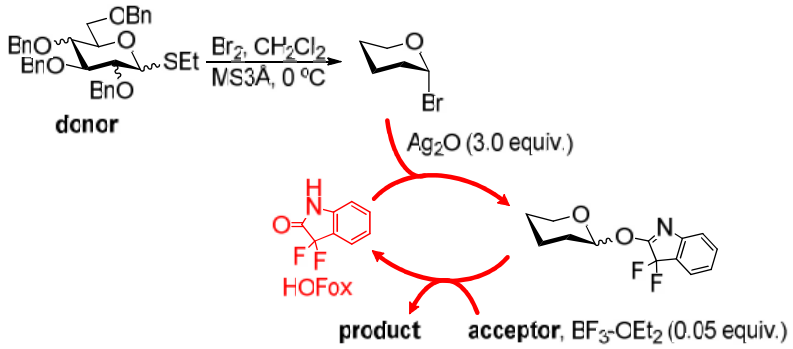
Entry	*Acceptor*	*Solvent*	*Product*	*Yield, %*[b]	*α/β ratio*[c]
1	2-propanol **26**	EtCN	 **27**	77	β only
2	**4**	CH_2Cl_2	 **5**	94	1/24
3	**4**	EtCN	**5**	99	β only
4	 **28**	CH_2Cl_2	 **29**	89	1/11
5	**28**	EtCN	**29**	87	1/18
6	 **30**	CH_2Cl_2	 **31**	85	1/12
7	**30**	EtCN	**31**	89	β only
8	 **32**	CH_2Cl_2	 **33**	94	1/4.0
9	**32**	EtCN	**33**	92	1/12
10	 **34**	CH_2Cl_2	 **35**	90	1/6.0
11	**34**	EtCN	**35**	88	1/15
12	 **36**	CH_2Cl_2	 **37**	86	β-only
13	 **38**	CH_2Cl_2	 **39**	88	1/23

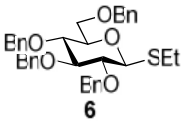
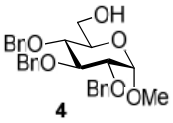
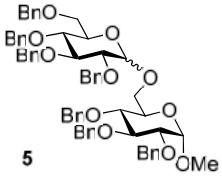
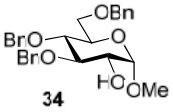
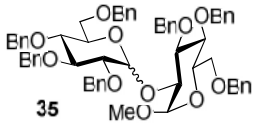
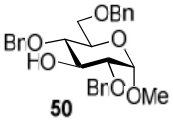
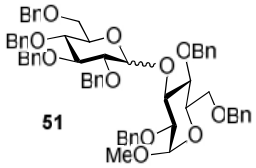
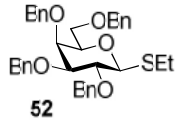
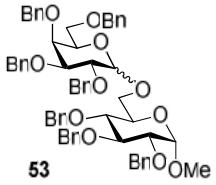
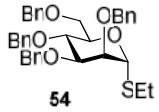
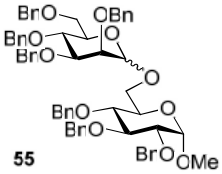
Table 9S. Glycosylation with per-acylated glucosyl, galactosyl, and mannosyl OFox donors in CH_2Cl_2 with TMSOTf as a promoter at rt.

Entry	*Donor*	*Acceptor*	*Product*	*Yield, %*
1[a]	 **14**	**4**	 **41**	80
2	 **16**	**4**	 **42**	94
3	**16**	**28**	 **43**	86
4	**16**	**30**	 **44**	90
5	**16**	**32**	 **45**	93
6	 **18**	**4**	 **46**	98
7	**18**	**30**	 **47**	98
9	 **20**	**4**	 **48**	93
10	**20**	**30**	 **49**	90

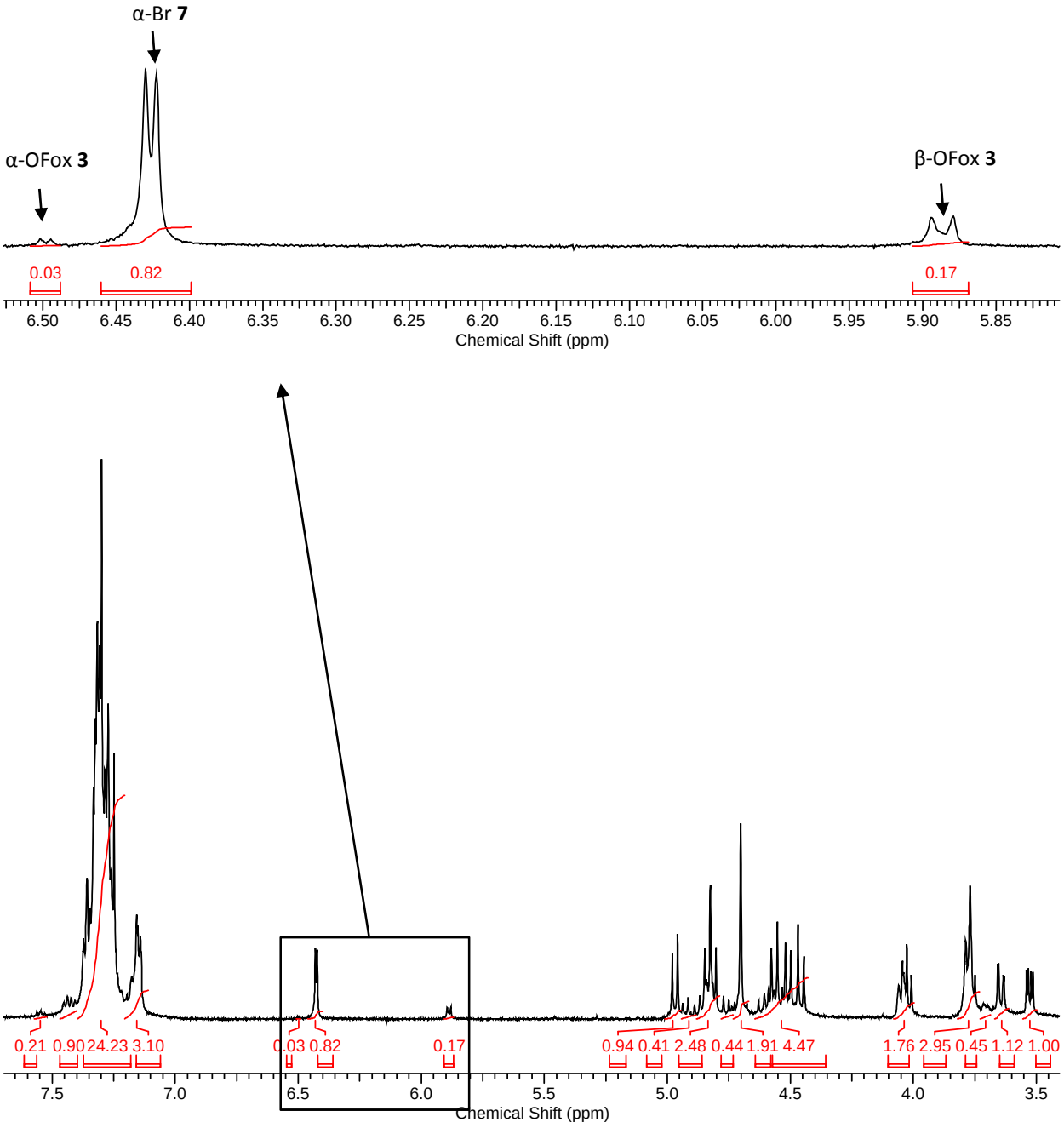
[a] – $SnCl_4$ was used as a promoter to prevent acetyl migration to the C-6 of acceptor that was observed in the presence of TMSOTf.

Table 10S. Regenerative glycosylation, a complete experimental dataset



Entry	*Donor*	*Acceptor*	*HOFox (equiv.)*	*Reaction time*	*Product*	*Yield*	*Ratio α/β*
1	 **6**	 **4**	0	5 h	 **5**	9%	1/1.1
2	**6**	**4**	0.10	3 h	**5**	84%	1/1.9
3	**6**	**4**	0.25	2 h	**5**	79%	1/1.9
4	**6**	**4**	0.50	40 min	**5**	86%	1/1.2
5	**6**	**4**	0.75	30 min	**5**	88%	1/1.2
6	**6**	**4**	1.0	10 min	**5**	90%	1/1.2
7	**6**	 **34**	0.1	3 h	 **35**	72%	1/1.7
8	**6**	 **50**	0.25	3 h	 **51**	62%	1/1.0
9	 **52**	**4**	0.1	2.5 h	 **53**	69%	1/1.1
10	 **54**	**4**	0.1	3 h	 **55**	75%	2.5/1

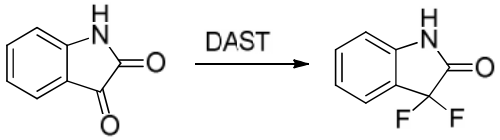
Scheme 1S. "Regenerative glycosylation" experiment performed in the NMR tube with bromide donor **7**, HOFox (0.25 equiv.), Ag_2O (3.0 equiv.) in CD_2Cl_2 at 0 ^oC in the absence of a glycosyl acceptor



General Experimental Remarks

All reactions were performed under argon with dry, freshly distilled solvents unless otherwise noted. CH_2Cl_2, $ClCH_2CH_2Cl$, toluene, CH_3CN, and EtCN were distilled from CaH_2 directly prior to application. Anhydrous 1,4-dioxane, tetrahydrofuran, and diethyl ether were used as is. AgOTf was co-evaporated with toluene (3 x 10 mL) and dried in *vacuo* for 2-3 h directly prior to application. TMSOTf, $SnCl_4$, MeOTf, BF_3-OEt_2, $Cu(OTf)_2$, $PdCl_2$, $TMSClO_4$ and $Bi(OTf)_3$ were used as is. Molecular sieves (3 Å or 4 Å), used for the reactions, were crushed and activated at 390 °C and then for 2-3 h at 390 °C prior to application. Reactions were monitored by TLC on Kieselgel 60 F_{254} and the compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at < 40 ^{o}C. Column chromatography was performed on silica gel 60 (70-230 mesh). Optical rotations were measured at 'Jasco P-1020' polarimeter. ^{1}H n.m.r. spectra were recorded at 300 MHz, 500 MHz, or 600 MHz. ^{13}C n.m.r. spectra were recorded at 75 MHz or 150 MHz. ^{19}F spectra were recorded at 282.2 MHz. The ^{1}H chemical shifts are referenced to the signal of the residual $CHCl_3$ (δ_H = 7.27 ppm) for solutions in $CDCl_3$. The ^{13}C chemical shifts are referenced to the central signal of $CDCl_3$ (δ_C = 77.23 ppm) for solutions in $CDCl_3$. HRMS determinations were made with the use of JOEL MStation (JMS-700) Mass Spectrometer.

Synthesis of 3,3-difluoroxindole (HOFox, 3,3-difluoroindolin-2-one)



The title compound was obtained from isatin and DAST as previously described. Analytical data were in accordance with that previously reported.[2]

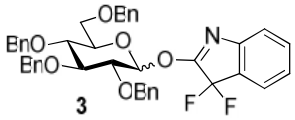
Preparation of OFox imidates

Method A. A typical procedure for the preparation from hemiacetals via glycosyl chlorides. $SOCl_2$ (81.1 µL, 1.11 mmol) was added dropwise to a solution of hemiacetal (**8** or **9**, 0.20 g, 0.37 mmol) in dry CH_2Cl_2 (2.0 mL) and dry DMF (14.3 µL) and the resulting mixture was stirred under argon for 7 h at rt. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (~30 mL) and washed with sat. aq. $NaHCO_3$ (2 x 15 mL) and cold water (2 x 15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue containing crude glycosyl halide (0.37 mmol) was dried under high vacuum for 4 h. Freshly activated molecular sieves (3 Å, 600 mg) and dry CH_2Cl_2 (2.0 mL) were added and the resulting mixture was stirred under argon for 1 h at rt. After that, 3,3-difluorooxindole (69 mg, 0.41 mmol), Ag_2O (258 mg, 1.11 mmol), and diisopropylethylamine (DIPEA, 97 µL, 0.56 mmol) were added and the resulting mixture was stirred for 8-12 h. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 15 mL) and water (2 x 15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-hexanes gradient elution) to afford the corresponding OFox imidates **3** or **10** in yields listed in Table 1S.

Methods B and C. A typical procedure for the preparation from glycosyl bromides. A mixture of a glycosyl bromide (**11**, **13**, **15** or **21**, 0.15 mmol) and freshly activated molecular sieves (3 Å, 300 mg) in dry CH_2Cl_2 (Method B, 1.0 mL) or toluene (Method C, 1.0 mL) was stirred under argon for 1 h at rt. After that, 3,3-difluorooxindole (25.7 mg, 0.15 mmol), Ag_2O (105 mg, 0.45 mmol), and DIPEA (39.7 µL, 0.23 mmol) were added and the resulting mixture was stirred for 40 min-10 h at the temperature indicated in Table 1S. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 15 mL) and water (2 x 15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-hexanes gradient elution) to afford the corresponding OFox imidates in yields listed in Table 1S.

Method D. A typical procedure for the preparation from pentabenzoates via glycosyl bromides. A 33% solution of HBr in AcOH (0.10 mL, 1.7 mmol) was added to a solution of a 1,2,3,4,6-penta-*O*-benzoyl-D-galacto or mannopyranose (**17** or **19**, 100 mg, 0.14 mmol) in dry CH_2Cl_2 (0.2 mL) and the resulting mixture was stirred under argon for 2-4 h at rt. The reaction mixture was then diluted with CH_2Cl_2 (~40 mL) and washed with cold sat. aq. $NaHCO_3$ (2 x 15 mL) and cold water (2 x 15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue containing crude glycosyl bromide (0.14 mmol) was dried under high vacuum for 4 h. After that, freshly activated molecular sieves (3 Å) and dry CH_2Cl_2 (1.4 mL) were added and the resulting mixture was stirred under argon for 1 h at rt. After that, the resulting mixture was cooled to 0 ^{o}C in case of galactose sugar and at rt for mannose sugar, followed by addition of 3,3-difluorooxindole (26.7 mg, 0.16 mmol), Ag_2O (99.2 mg, 0.43 mmol) and DIPEA (37.4 µL, 0.21 mmol) were added and the resulting mixture was stirred for 2-6 h as indicated in Table 1S. The solids were then filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 15 mL) and water (2 x 15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-hexanes gradient elution) to afford the corresponding OFox imidates in yields listed in Table 1S.

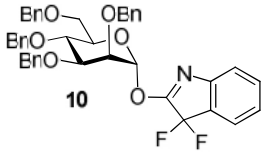
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3)



3

The title compound was obtained from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **8**[3] by Method B in 62% yield (α/β = 10/1) as a white foam. Analytical data for α-**3**: R_f = 0.43 (ethyl acetate/hexanes, 1/4, v/v); ^{1}H n.m.r. (300 MHz): δ, 3.66 (dd, 1H, $J_{5,6a}$ = 1.8 Hz, $J_{6a,6b}$ = 10.9 Hz, H-6a), 3.79 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2,), 3.79 (dd, 1H, $J_{5,6b}$ = 3.3 Hz, H-6b), 3.83 (dd, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 4.01 (m, 1H, H-5), 4.13 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 4.52 (dd, 2H, ^2J = 12.0 Hz, CH_2Ph), 4.69 (dd, 2H, ^2J = 10.5 Hz, CH_2Ph), 4.73 (s, 2H, CH_2Ph), 4.93 (dd, 2H, ^2J = 10.9 Hz, CH_2Ph), 6.50 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 7.11-7.42 (m, 24H, aromatic) ppm; ^{13}C n.m.r. (75 MHz): δ, 68.1, 73.2, 73.5, 73.6 (x 2), 75.2, 75.3, 79.4, 81.5, 99.8, 117.4, 120.4, 123.3, 125.7, 127.8, 127.9, 128.0 (x 4), 128.0 (x 2), 128.1 (x 7), 128.6 (x 8), 133.6, 137.9, 138.0, 138.2, 138.8 ppm; ^{19}F n.m.r.: δ, -121.3 (s, 2F, CF_2) ppm; HR-FAB MS $[M+Na]^+$ calculated for $C_{42}H_{39}F_2NO_6Na^+$ 714.2643, found 714.2645.

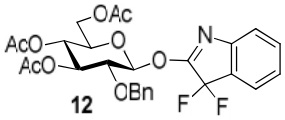
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (10)



10

The title compound was obtained from 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranose **9**[4] by Method A in 61% yield as a white foam. Analytical data for **10**: R_f = 0.45 (ethyl acetate/hexanes, 2/3, v/v); $[\alpha]_D^{24}$ +13.7 (*c* = 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 3.74 (dd, 1H, $J_{5,6a}$ = 1.8 Hz, $J_{6a,6b}$ = 11.3 Hz, H-6a), 3.84 (dd, 1H, $J_{5,6b}$ = 4.3 Hz, H-6b), 3.95-4.03 (m, 3H, H-2, 4, 5), 4.14 (m, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 4.60 (dd, 2H, ^2J = 11.6 Hz, CH_2Ph), 4.62 (dd, 2H, ^2J = 12.1 Hz, CH_2Ph), 4.70 (dd, 2H, ^2J = 10.7 Hz, CH_2Ph), 4.78 (s, 2H, CH_2Ph), 6.40 (d, 1H, $J_{1,2}$ = 1.1 Hz, H-1), 7.15-7.47 (m, 24H, aromatic) ppm; ^{13}C n.m.r. (75 MHz): δ, 69.1, 72.6, 72.8, 73.1, 73.4, 74.0, 74.8, 75.3, 79.0, 97.7, 120.5 (x 2), 123.4 (x 2), 125.9, 126.7, 127.7, 127.7 (x 2), 128.0 (x 3), 128.1 (x 2), 128.2 (x 2), 128.3 (x 3), 128.5 (x 2), 128.6 (x 6), 133.7, 138.0, 138.2, 138.4 (x 2), ppm; ^{19}F n.m.r.: δ, -121.5 (s, 2F, CF_2) ppm; HR-FAB MS $[M+Na]^+$ calculated for $C_{42}H_{39}F_2NO_6Na^+$ 714.2643, found 714.2639.

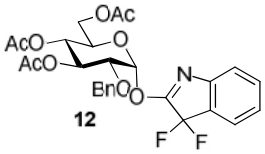
3,3-Difluoro-3*H*-indol-2-yl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-β-D-glucopyranoside (β-12)



12

The title compound was obtained from 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl bromide **11** by Method B at rt in 80% yield as a white foam. Analytical data for β-**12**: R_f = 0.39 (ethyl acetate/hexanes, 2/3, v/v); $[\alpha]_D^{26}$ +13.7 (*c* = 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 1.95, 2.03, 2.07 (3s, 9H, 3 x $COCH_3$), 3.80 (dd, 1H, $J_{2,3}$ = 7.9 Hz, H-2), 3.95 (m, 1H, H-5), 4.14 (dd, 1H, $J_{5,6a}$ = 2.3 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6a), 4.34 (dd, 1H, $J_{5,6b}$ = 4.4 Hz, H-6b), 4.74 (dd, 2H, ^2J = 11.6 Hz, CH_2Ph), 5.11 (dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 5.27 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 5.94 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 7.18-7.49 (m, 9H, aromatic) ppm; ^{13}C n.m.r. (75 MHz): δ, 20.7 (x 2), 20.8, 61.5, 67.9, 72.6, 73.6, 74.7, 77.6, 99.1, 120.6, 123.3, 126.2, 128.1 (x 2), 128.3 (x 3), 128.5 (x 3), 133.7, 137.1, 150.3, 169.7, 170.0, 170.7 ppm; ^{19}F n.m.r.: δ, -122.0 (d, 2F, CF_2) ppm; HR-FAB MS $[M+Na]^+$ calculated for $C_{27}H_{27}F_2NO_9Na^+$ 570.1552, found 570.1562.

3,3-Difluoro-3*H*-indol-2-yl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranoside (α-12)

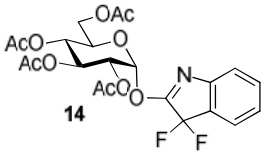


12

The title compound was obtained from 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl bromide **11** by Method B at 0 ^oC in 81% yield as a white foam. Analytical data for α-**12**: R_f = 0.38 (ethyl acetate/hexanes, 2/3, v/v); $[\alpha]_D^{25}$ +101.4 (*c* = 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 2.02, 2.03, 2.05 (3s, 9H, 3 x $COCH_3$), 3.81 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 4.06 (dd, 1H, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.18 (m, 1H, H-5), 4,29 (dd, 1H, $J_{5,6b}$ = 4.1 Hz, H-6b), 4.67 (s, 2H, CH_2Ph), 5.11 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 5.57 (d, 1H, $J_{3,4}$ = 9.7 Hz, H-3), 6.45 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 7.17-7.40 (m, 9H, aromatic) ppm; ^{13}C n.m.r. (75 MHz): δ, 20.7 (x 2), 20.8, 61.4, 67.8, 69.8, 71.4, 73.3, 75.7, 95.0, 120.4, 123.3, 125.9, 126.8, 127.9 (x 3), 128.2, 128.6 (x 3),

133.5, 137.2, 150.4, 168.7, 169.8, 170.1 ppm; ^{19}F n.m.r.: δ, -121.6 (s, 1F, CF_2^a), -121.5 (s, 1F, CF_2^b); HR-FAB MS $[M+Na]^+$ calculated for $C_{27}H_{27}F_2NO_9Na^+$ 570.1552, found 570.1569.

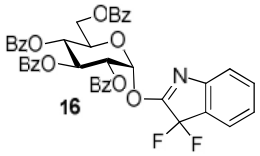
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (14)



14

The title compound was obtained from 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide **13**[5] by Method C in 62% yield as a white foam. Analytical data for **14**: R_f = 0.42 (ethyl acetate/hexanes, 1/1, v/v); $[\alpha]_D^{21}$ +5.2 (*c*= 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 1.96, 1.97, 1.98, 2.01 (4s, 12H, 4 x $COCH_3$), 3.95 (m, 1H, H-5), 4.15 (dd, 1H, $J_{5,6a}$ = 2.3 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6a), 4.30 (dd, 1H, $J_{5,6b}$ = 4.3 Hz, H-6b), 5.17-5.32 (m, 3H, H-2, 3, 4), 5.95 (m, 1H, H-1), 7.14-7.40 (m, 4H, aromatic) ppm; ^{13}C n.m.r. (75 MHz): δ, 20.4, 20.6 (x 2), 20.7, 61.4, 67.6, 70.3, 72.4, 72.9, 96.6, 120.5 (x 2), 123.3 (x 2), 126.2, 126.8, 133.6, 150.0, 169.3, 169.4, 170.2, 170.8 ppm; ^{19}F n.m.r.: δ, -122.4 (s, 1F, CF_2^a), -122.3 (s, 1F, CF_2^b) ppm; HR-FAB MS $[M+H]^+$ calculated for $C_{22}H_{23}F_2NO_{10}$ 500.1290, found 500.1361.

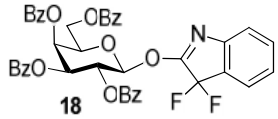
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranoside (16)



16

The title compound was obtained from 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide **15**[6] by Method B in 75% yield as a pale yellow foam. Analytical data for **16**: R_f = 0.41 (ethyl acetate/hexanes, 3/7, v/v); $[\alpha]_D^{23}$ +45.8 (*c*= 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 4.48 (dd, 1H, $J_{5,6a}$ = 4.7 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.64 (m, 2H, $J_{5,6b}$ = 2.3 Hz, H-5, 6b), 5.69 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 5.83 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 6.31 (dd, 1H, $J_{3,4}$ = 10.0 Hz, H-3), 6.82 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 7.05-7.99 (m, 24H, aromatic) ppm; ^{13}C n.m.r. (75 MHz): δ, 62.4, 68.6, 70.1, 70.3, 70.6, 94.8, 120.6, 123.2, 126.0, 126.5, 128.3, 128.4 (x 2), 128.4 (x 2), 128.5 (x 4), 128.6 (x 2), 128.8, 129.1, 129.5, 129.7 (x 2), 129.8 (x 2), 130.0 (x 4), 133.1, 133.4 , 133.5, 133.6, 133.7, 150.1, 165.2, 165.5, 165.6, 166.0 ppm; ^{19}F n.m.r.: δ, -121.8 (s, 1F, CF_2^a), -121.6 (s, 1F, CF_2^b) ppm; HR-FAB MS $[M+Na]^+$ calculated for $C_{42}H_{31}F_2NO_{10}Na^+$ 770.1813, found 770.1800.

3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (18)

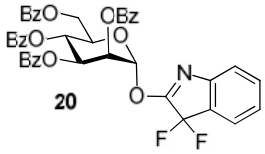


18

This compound was obtained from 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide **17**[7] by Method D in 75% yield as a white foam. Analytical data for **18**: R_f = 0.39 (ethyl acetate/hexanes, 3/7, v/v); $[\alpha]_D^{22}$ +2.7 (*c*= 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 4.51 (dd, 1H, $J_{5,6a}$ = 5.9 Hz, $J_{6a,6b}$ = 10.6 Hz, H-6a), 4.63 (m, 1H, H-5), 4.72 (dd, 1H, $J_{5,6b}$ = 6.6 Hz, H-6b), 5.75 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 6.11 (m, 2H, H-2, 4), 6.34 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 7.14-8.14 (m, 24H, aromatic) ppm; ^{13}C n.m.r. (75 MHz): δ, 61.8, 67.6, 68.9, 71.4, 72.7, 97.4, 120.4, 123.6, 124.7, 125.4, 128.3, 128.6 (x 4), 128.7, 128.8, 128.9 (x 2), 129.0, 129.2 (x 2), 129.4, 129.9 (x 9),

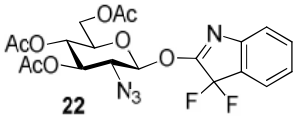
130.1 (x 2), 133.3, 133.5, 133.6, 133.8, 165.1, 165.5 (x 2), 166.0 ppm; ^{19}F n.m.r.: δ, -122.2 (s, 2F, CF_2); HR-FAB MS $[M+Na]^+$ calculated for $C_{42}H_{31}F_2NO_{10}Na^+$ 770.1813, found 770.1791.

3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (20)



The title compound was obtained from 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide **19**[8] by Method D in 84% yield as a white foam. Analytical data for **20**: R_f = 0.43 (ethyl acetate/hexanes, 3/7, v/v); $[\alpha]_D^{21}$ -5.3 (*c* = 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 4.52 (dd, 1H, $J_{5,6a}$ = 4.4 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 4.62 (m, 1H, H-5), 4.70 (dd, 1H, $J_{5,6b}$ = 2.2 Hz, H-6b), 6.02 (dd, 1H, $J_{2,3}$ = 3.3 Hz, H-2), 6.07 (dd, 1H, $J_{3,4}$ = 10.0 Hz, H-3), 6.24 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 6.64 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 7.16-8.09 (m, 24H, aromatic) ppm; ^{13}C n.m.r. (75 MHz): δ, 62.5, 66.2, 69.0, 69.6, 71.5, 96.0, 121.0, 123.5, 125.5, 126.4, 126.8, 128.4, 128.5 (x 2), 128.6 (x 2), 128.7 (x 2), 128.8, 128.9 (x 2), 128.9, 129.0, 129.2, 129.8, 129.9 (x 2), 130.0 (x 2), 130.1 (x 4), 133.2, 133.6, 133.8, 134.0, 138.1, 165.2, 165.5, 165.6, 166.1 ppm; ^{19}F n.m.r.: δ, -121.8 (s, 1F, CF_2^a), -121.5 (s, 1F, CF_2^b); HR-FAB MS $[M+Na]^+$ calculated for $C_{42}H_{31}F_2NO_{10}Na^+$ 770.1813, found 770.1814.

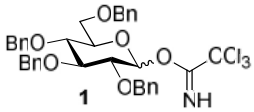
3,3-Difluoro-3*H*-indol-2-yl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (22)



The title compound was obtained from 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl bromide **21** by Method B in 70% yield as a white foam. Analytical data for **22**: R_f = 0.43 (ethyl acetate/hexanes, 2/3, v/v); $[\alpha]_D^{24}$ +8.4 (*c*= 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 2.05, 2.08, 2.12 (3s, 9H, 3 x $COCH_3$), 3.88 (dd, 1H, $J_{2,3}$ = 9.2 Hz, H-2), 3.93 (m, 1H, H-5), 4.16 (dd, 1H, $J_{5,6a}$ = 2.3 Hz, H-6a), 4.35 (dd, 1H, $J_{5,6b}$ = 4.3 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6b), 5.13 (dd, 1H, $J_{4,5}$ = 8.9 Hz, H-4), 5.17 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 5.82 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1), 7.19-7.43 (m, 4H, aromatic) ppm; ^{13}C n.m.r. (75 MHz): δ, 20.7, 20.8, 20.9, 60.6, 63.1, 67.8, 72.7, 73.0, 97.6, 120.7, 123.5, 126.5, 126.7, 127.0, 127.3, 133.8, 150.1, 169.8, 170.0, 170.7 ppm; ^{19}F n.m.r.: δ, -122.2 (s, 2F, CF_2). HR-FAB MS $[M+Na]^+$ calculated for $C_{20}H_{20}F_2N_4O_8Na^+$ 505.1147, found 505.1142.

Preparation and characterization of other glycosyl donors and intermediates

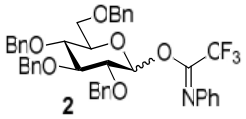
2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl trichloroacetimidate (1)



This compound was obtained from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **8**[3] in 62% yield as a white foam as previously described.[9] Analytical data for is this for α-**1**: R_f = 0.43 (ethyl acetate/hexanes, 1/4 v/v); ^{1}H n.m.r. (300 MHz): δ, 3.67 (dd, 1H, $J_{5,6a}$ = 1.9 Hz, $J_{6a,6b}$ = 10.9 Hz, H-6a), 3.74-3.80 (m, 3H, H-2, 4, 6b), 3.99 (m, 1H, H-5), 4.05 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 4.53 (dd, 2H, ^2J = *12*.0 Hz, CH_2Ph), 4.71 (dd, 2H, ^2J = 11.7 Hz, CH_2Ph), 4.73 (dd, 2H, ^2J = 10.7 Hz,

C*H*$_2$Ph), 4.84 (dd, 2H, ^2J = 7.6 Hz, C*H*$_2$Ph) , 6.50 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 7.12-7.33 (m, 24H, aromatic), 8.57 (s, 1H, NH) ppm; ^{13}C n.m.r. (75 MHz): δ, 68.1, 73.0, 73.2, 73.6, 75.5, 75.8, 79.5, 81.5, 91.4, 94.5, 127.8 (x 3), 127.9 (x 2), 128.0, 128.1 (x 2), 128.2 (x 4), 128.5 (x 4), 128.6 (x 4), 137.9, 138.1, 138.2, 138.7, 161.4 ppm; HR-ESI MS $[M+Na]^+$ calculated for $C_{36}H_{36}Cl_3NO_6Na^+$ 706.1506, found 706.1500.

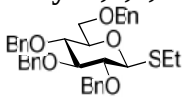
2,3,4-Tri-*O*-benzyl-α,β-D-glucopyranosyl *N*-phenyltrifluoroacetimidate (2)



2

The title compound was obtained from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **8**[3] by adapting previously published procedure.[10] 2,2,2-Trifluoro-*N*-phenylethanimidoyl chloride (89.4 µL, 0.55 mmol) and K_2CO_3 (55 mg, 0.55 mmol) were added to a solution of **8** (150 mg, 0.28 mmol) in acetone (1.5 mL) and the resulting mixture was stirred for 3 h at rt. The solids were filtered off through a pad of Celite and the filtrate was concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-hexanes gradient elution) to afford the title compound in 72% yield as a white amorphous solid. Analytical data for β-**2**: R_f = 0.5 (ethyl acetate/hexanes, 1/4, v/v); ^{1}H n.m.r. (500 MHz): δ, 3.56-3.95 (m, 6H, H-2, 3, 4, 5, 6a, 6b), 4.58 (dd, 2H, ^2J = 9.5 Hz, C*H*$_2$Ph), 4.69 (dd, 2H, ^2J = 12.2 Hz, C*H*$_2$Ph), 4.88 (s, 2H, C*H*$_2$Ph), 5.00 (dd, 2H, ^2J = 10.2 Hz, C*H*$_2$Ph) , 5.74 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 6.78-7.5 (m, 25H, aromatic); ^{13}C n.m.r. (75 MHz): δ, 73.6, 75.3, 75.4, 75.8 (x 2), 75.9 (x 2), 75.8, 81.1, 84.7, 119.5, 124.5, 127.9, 128.0 (x 2), 128.1 (x 3), 128.2 (x 3), 128.4 (x 2), 128.6 (x 6), 128.7 (x 7), 128.9 (x 2), 137.9, 138.1 (x 2), 138.5, 143.6 ppm; HR-FAB MS $[M+Na]^+$ calculated for $C_{42}H_{40}F_3NO_6Na^+$ 734.2705, found 734.2720.

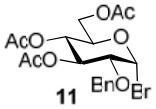
Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (6)



6

The title compound was obtained as previously described.[11]

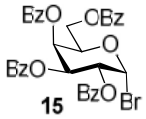
3,4,6-Tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl bromide (11)



11

The title compound was obtained from 1,3,4,6-tetra-*O*-acetyl-2-*O*-benzyl-D-glucopyranose[12] in 90% yield as a white foam as previously described.[13] Analytical data for **11**: R_f = 0.43 (ethyl acetate/hexanes, 2/3, v/v); ^{1}H n.m.r. (300 MHz): δ, 1.96, 1.98, 2.00 (3s, 9H, 3 x COC*H*$_3$), 3.57 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 4.12 (m, 1H, $J_{5,6a}$ = 4.1 Hz, H-6a), 4.22 (m, 1H, H-5), 4.27 (dd, 1H, $J_{5,6b}$ = 4.0 Hz, $J_{6a,6b}$ = 12.6 Hz, 6b), 4.63 (dd, 2H, ^2J = 12.3 Hz, C*H*$_2$Ph), 5.06 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 5.48 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 6.34 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1) ppm; ^{13}C n.m.r. (75 MHz): δ, 20.8, 20.9 (x 2), 61.3, 67.3, 72.2 (x 2), 72.9, 76.5, 89.2, 128.1 (x 2), 128.5, 128.8 (x 2), 137.0, 169.9, 170.1, 170.7 ppm; HR-FAB MS $[M+Na]^+$ calculated for $C_{19}H_{23}BrO_8Na^+$ 481.0474, found 481.0483.

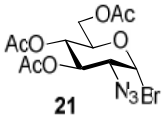
2,3,4,6-Tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (15)



15

The title compound was obtained from 1,2,3,4,6-penta-*O*-benzoyl-D-galactopyranose in 90% yield as a white foam as previously described.[14] Analytical data for **15**: R_f = 0.44 (ethyl acetate/hexanes, 3/7, v/v); $[\alpha]_D^{21}$ +152.5 (*c*= 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 4.47 (dd, 1H, $J_{5,6b}$ = 6.0 Hz, $J_{6a,6b}$ = 11.6 Hz, H-6b), 4.65 (dd, 1H, $J_{5,6a}$ = 6.8 Hz, H-6a), 4.93 (dd, 1H, H-5), 5.67 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 6.06 (dd, 1H, $J_{3,4}$ = 10.0 Hz, H-3), 6.13 (dd, 1H, $J_{4,5}$ = 3.8 Hz, H-4), 6.98 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1) ppm; ^{13}C n.m.r. (75 MHz): δ, 61.9, 68.3, 68.8, 69.1, 72.0, 88.5, 128.6 (x 2), 128.7 (x 2), 128.7, 128.8 (x 2), 128.9 (x 2), 129.0 (x 2), 129.4, 130.0 (x 4), 130.2 (x 4), 133.6 (x 2), 134.0 (x 2), 165.5, 165.6, 165.8, 166.1 ppm; HR-FAB MS $[M+Na]^+$ calculated for $C_{34}H_{27}BrO_9Na^+$ 681.0736, found 681.0721.

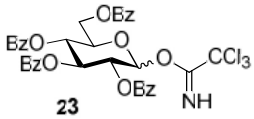
3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl bromide (21)



21

The title compound was obtained from 1,3,4,6-tetra-*O*-acetyl-2-azido-2-deoxy-D-glucopyranose[15,16] in 90% yield as a white foam as previously described.[17,18] Analytical data for **21**: R_f = 0.46 (ethyl acetate/hexanes, 2/3, v/v); $[\alpha]_D^{19}$ +146.9 (*c*= 1.0, $CHCl_3$); ^{1}H n.m.r. (300 MHz): δ, 2.06, 2.09, 2.11 (3s, 9H, 3 x $COCH_3$), 3.81 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 4.12 (m, 1H, $J_{5,6a}$ = 1.9 Hz, $J_{6a,6b}$ = 8.5 Hz, H-6a), 4.33 (m, 2H, $J_{5,6b}$ = 4.1 Hz, H-5, 6b), 5.14 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 5.5 (dd, 1H, $J_{3,4}$ = 10.0 Hz, H-3), 6.42 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1) ppm; ^{13}C n.m.r. (75 MHz): δ, 20.5, 20.6 (x 2), 61.0, 62.3, 67.3, 71.7, 72.4, 87.4, 169.6, 169.7, 170.4 ppm; HR-FAB MS $[M+Na]^+$ calculated for $C_{12}H_{16}BrN_3O_7Na^+$ 416.0069, found 416.0065.

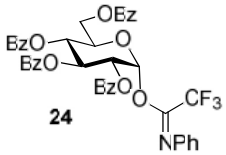
2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (23)



23

The title compound was obtained from 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose **25**[1] in 83% yield as a white foam as previously described.[1] Analytical data for **23** was in accordance with that reported previously.[19]

2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl N-phenyltrifluoroacetimidate (24)

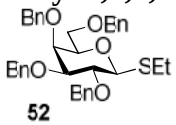


24

The title compound was obtained from 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose **25**[1] by adapting previously published procedure.[10] 2,2,2,-Trifluoro-*N*-phenylethanimidoyl chloride (0.70 mL, 4.37 mmol) and K_2CO_3 (0.54 g, 5.46 mmol) were added to a solution of **25** (2.17 g, 3.64 mmol) in acetone (25 mL) and the resulting mixture was stirred for 5 h at rt. The solids were filtered off through a pad of Celite and the filtrate was concentrated in *vacuo*. The residue was purified by

column chromatography on silica gel (ethyl acetate-hexanes gradient elution) to afford the title compound in 86% yield as a white foam. Analytical data for α-**24**: R_f = 0.5 (ethyl acetate/hexanes, 3/7, v/v); $[\alpha]_D^{27}$ +49.4 (*c*= 1.0, $CHCl_3$); ^{1}H n.m.r. (500 MHz): δ, 4.51 (dd, 1H, $J_{5,6a}$ = 4.4 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6a), 4.69 (m, 1H, H-5), 4.77 (dd, 1H, $J_{5,6b}$ = 1.8 Hz, H-6b), 5.67 (dd, 1H, $J_{2,3}$ = 10.3 Hz, H-2), 5.93 (dd, 1H, $J_{4,5}$ = 10.1 Hz, H-4), 6.30 (m, 3H, H-3, 2', 6'), 6.92 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 7.00-8.15 (m, 25H, aromatic) ppm; ^{13}C n.m.r. (125 MHz): δ, 62.4, 68.6, 70.0, 70.5, 70.8, 92.3, 119.1, 124.4, 128.6 (x 2), 128.7 (x 5), 128.8 (x 5), 128.9, 129.7, 129.9 (x 2), 130.0 (x 8), 133.3, 133.4, 133.7, 133.8, 142.8, 143.0, 165.2, 165.4, 165.7, 166.1; ^{19}F n.m.r.: δ, -65.51 (s, 3F, CF_3) ppm; HR-FAB MS $[M+Na]^+$ calculated for $C_{42}H_{31}F_2NO_{10}Na^+$ 790.1876, found 790.1886.

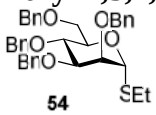
Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (52)



52

The title compound was obtained as previously described.[20]

Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyranoside (54)



54

The title compound was obtained as previously described.[21]

General glycosylation procedures

Method A. *A typical TMSOTf-promoted glycosylation procedure.* A mixture of glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (4Å, 90 mg) in CH_2Cl_2 (0.5 mL) or other solvent as indicated in Tables was stirred under argon for 1 h at rt. The mixture was cooled to -78 ^{o}C or other temperature as indicated in Tables, TMSOTf (0.0055-0.011 mmol) was added, and the resulting mixture was stirred for 10-15 min as indicated in Tables. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford a glycoside derivative in yields listed in Tables.

Method B. *A typical BF_3-OEt_2-promoted glycosylation procedure.* A mixture of 3,3-difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **3** (32.7 mg, 0.047 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **4** (18.3 mg, 0.043 mmol), and freshly activated molecular sieves (4Å, 95 mg) in CH_2Cl_2 (0.6 mL) was stirred under argon for 1 h at rt. The mixture was cooled to -78 ^{o}C, BF_3-OEt_2 (0.3 μL, 0.002 mmol) was added, and the resulting mixture was stirred for 5 min. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and

concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford disaccharide **5** in 93% yield (α/β = 1/20, Table 6S).

Method C. *A typical $Cu(OTf)_2$-promoted glycosylation procedure.* A mixture of donor **3** (38.3 mg, 0.055 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **4** (23.4 mg, 0.05 mmol), and freshly activated molecular sieves (3 Å, 110 mg) in CH_2Cl_2 (0.64 mL) was stirred under argon for 1 h at rt. *$Cu(OTf)_2$* (2.0 mg, 0.003 mmol) was added and the resulting mixture was stirred for 5 min. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford disaccharide **5** in 97% yield (β only, Table 6S).

Method D. *A typical MeOTf-promoted glycosylation procedure.* A mixture of donor **3** (30.6 mg, 0.044 mmol), acceptor **4** (18.7 mg, 0.040 mmol), and freshly activated molecular sieves (4Å, 90 mg) in CH_2Cl_2 (0.5 mL) was stirred under argon for 1 h at rt. MeOTf (0.55 μL, 0.0044 mmol) was added and the resulting mixture was stirred for 10 min. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford disaccharide **5** in 91% yield (α/β = 1/>25, Table 6S)

Method E. *A typical AgOTf-promoted glycosylation procedure.* A mixture of donor **3** (43.5 mg, 0.062 mmol), acceptor **4** (26.7 mg, 0.057 mmol), and freshly activated molecular sieves (4Å, 120 mg) in CH_2Cl_2 (0.73 mL) was stirred under argon for 1 h at rt. AgOTf (7.3 mg, 0.028 mmol) was added and the resulting mixture was stirred for 24 h. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford disaccharide **5** in 71% yield (α/β = 1/1.6, Table 6S).

Method F. *A typical $PdCl_2$-promoted glycosylation procedure.* A mixture of donor **3** (33.2 mg, 0.048 mmol), acceptor **4** (20.3 mg, 0.044 mmol), and freshly activated molecular sieves (4Å, 90 mg) in CH_2Cl_2 (0.55 mL) was stirred under argon for 1 h at rt. $PdCl_2$ (2.55 mg, 0.014 mmol) was added and the resulting mixture was stirred for 36 h. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford disaccharide **5** in 57% yield (α/β = 1/1.7, Table 6S).

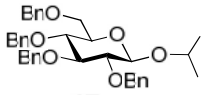
Method G. *A typical $TMSClO_4$-promoted glycosylation procedure.* A mixture of donor **3** (0.044 mmol), acceptor **4** (0.040 mmol), and freshly activated molecular sieves (3 Å, 90 mg) in Et_2O (0.5 mL) or Et_2O/1.4-dioxane (0.5 mL, 1/1, v/v) was stirred under argon for 1 h at rt. $TMSClO_4$[22]

(0.0044 mmol) was added and the resulting mixture was stirred for 5 min. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford disaccharide **5** in 75% (α/β = 5/1, Table 6S) or 54% yield (α/β = 6.2/1), respectively.

Method H. *A typical $Bi(OTf)_3$-promoted glycosylation procedure.* A mixture of donor **3** (41.3 mg, 0.059 mmol), acceptor **4** (25.2 mg, 0.054 mmol), and freshly activated molecular sieves (4Å, 120 mg) in CH_2Cl_2 (0.7 mL) was stirred under argon for 1 h at rt. The reaction was cooled to -60 ^oC followed by the addition of *$Bi(OTf)_3$* (3.9 mg, 0.006 mmol) and the resulting mixture was stirred for 20 min. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford disaccharide **5** in 85% yield, (α/β = 1/7.0, Table 6S).

Method I. *A typical $SnCl_4$-promoted glycosylation procedure.* A mixture of 3,3-difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside **14** (25.8 mg, 0.051 mmol), acceptor **4** (21.8 mg, 0.046 mmol), and freshly activated molecular sieves (4Å, 90 mg) in CH_2Cl_2 (0.5 mL) was stirred under argon for 1 h at rt. $SnCl_4$ (0.6 µL, 0.005 mmol) was added and the resulting mixture was stirred for 10 min (Table 4). The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford disaccharide **41** in 80% yield (Table 9S).

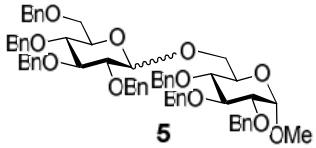
2-Propyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (27)



27

The title compound was obtained by Method A from donor **3** and isopropanol **26** as a white amorphous solid in 77% yield (β only). Analytical data for **27** was in accordance with that reported previously.[23]

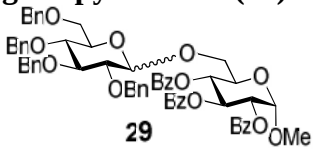
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (5)



5

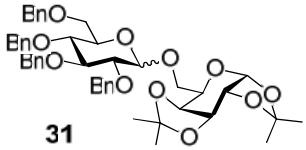
The title compound was obtained by Methods A-H from donor **3** and acceptor **4**[24] in 54-97% yield (α/β ranging from 6.2/1 to β-only, see Tables). Analytical data for **5** was in accordance with that reported previously.[25,26]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (29)



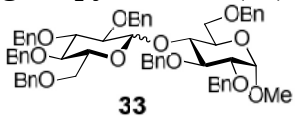
The title compound was obtained by Method A from donor **3** and methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside **28**[27] in CH_2Cl_2 or EtCN in 89% (α/β = 1/11) or 87% yield (α/β = 1/18), respectively. Analytical data for **29** was in accordance with that reported previously.[28]

6-*O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (31)



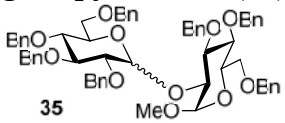
The title compound was obtained by Method A from donor **3** and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **30** in CH_2Cl_2 or EtCN in 85% (α/β = 1/12) or 89% yield (β only), respectively. Analytical data for **31** was in accordance with that reported previously.[29]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (33)



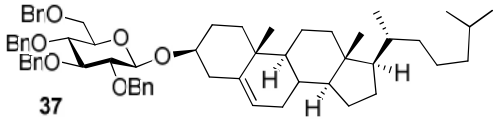
The title compound was obtained by Method A from donor **3** and methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside **32**[24] in CH_2Cl_2 or EtCN in 94% (α/β = 1/4) or 92% yield (α/β = 1/12), respectively. Analytical data for **33** was in accordance with that reported previously.[28]

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (35)



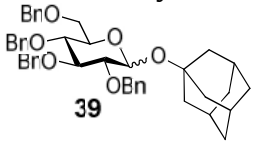
The title compound was obtained by Method A from donor **3** and methyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside **34**[24] in CH_2Cl_2 or EtCN in 90% (α/β = 1/6.0) or 88% yield (α/β = 1/15), respectively. Analytical data for **35** was in accordance with that reported previously.[30]

(3β)-Cholest-5-en-3-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranoside (37)



The title compound was obtained by Method A from donor **3** and (3β)-cholest-5-en-3-ol **36** as a white amorphous solid in 86% yield (β-only). Analytical data for **37** was in accordance with that reported previously.[31]

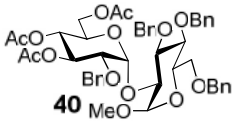
1-Adamantyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside (39)



39

The title compound was obtained by Method A from donor **3** and 1-adamantol **38** as a white amorphous solid in 88% yield (α/β = 1/23). Analytical data for **39** was in accordance with that reported previously.[31]

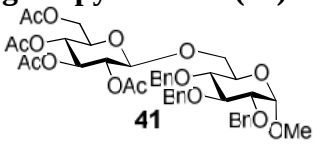
Methyl 2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (40)



40

The title compound was obtained by Method A from donor α-**12** or donor β-**12** and acceptor **34**[24] as a clear film in 89% or 88% yield (α only), respectively. Analytical data for **40** was in accordance with that reported previously.[30]

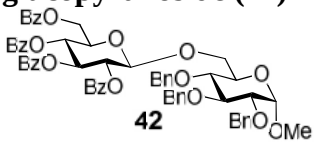
Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (41)



41

The title compound was obtained by Method I from donor **14** and acceptor **4**[24] as a clear film in 80% yield. Analytical data for **41** were essentially the same as reported previously.[32]

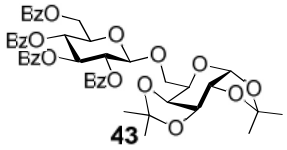
Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (42)



42

The title compound was obtained by Method A from donor **16** and acceptor **4**[24] as a clear film in 94% yield. Analytical data for **42** were essentially the same as reported previously.[24]

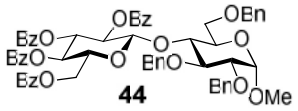
6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (43)



43

The title compound was obtained by Method A from donor **16** and acceptor **30** in 86% yield. Analytical data for **43** were essentially similar as reported previously.[30]

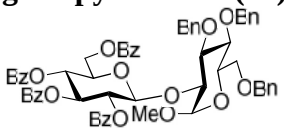
Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (44)



44

The title compound was obtained by Method A from donor **16** and acceptor **32**[24] as a clear film in 90% yield. Analytical data for **44** were essentially the same as reported previously.[24]

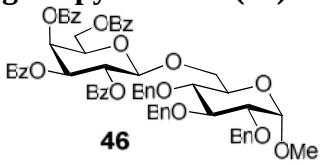
Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (45)



45

The title compound was obtained by Method A from donor **16** and acceptor **34**[24] as a clear film in 93% yield. Analytical data for **45** were essentially the same as reported previously.[24]

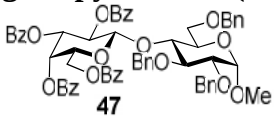
Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (46)



46

The title compound was obtained by Method A from donor **18** and acceptor **4**[24] as a clear film in 98% yield. Analytical data for **46** were essentially the same as reported previously.[33]

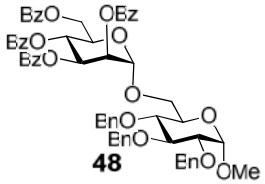
Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (47)



47

The title compound was obtained by Method A from donor **18** and acceptor **32**[24] as a clear film in 98% yield. Analytical data for **47** were essentially the same as reported previously.[30]

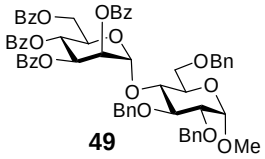
Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (48)



48

The title compound was obtained by Method A from donor **20** and acceptor **4**[24] as a clear film in 93% yield. Analytical data for **48** were essentially the same as reported previously.[30]

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (49)



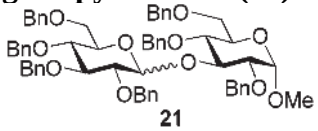
49

The title compound was obtained by Method A from donor **20** and acceptor **32**[24] as a clear film in 90% yield. Analytical data for **49** were essentially the same as reported previously.[34]

A typical procedure for regenerative glycosylation

A mixture of ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside **6**[11] (30 mg, 0.051 mmol) and activated molecular sieves (3 Å, 90 mg) in CH_2Cl_2 (0.5 mL) was stirred under argon for 1 h at rt. The mixture was cooled to 0 ^oC, bromine (0.27 μL, 0.01 mmol) was added, and the resulting mixture was kept for 15 min at 0 ^oC. After that, 3,3-difluorooxindole (0.9 mg - 8.9 mg, 0.0051-0.051 mmol, see Table 2 of the manuscript), and Ag_2O (36 mg, 0.16 mmol) were added to the reaction mixture and the resulting mixture was stirred for 10 min - 1 h at 0 ^oC. Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **4** (18.3 mg, 0.039 mmol) and BF_3-OEt_2 (0.33 μL, 0.0025 mmol) were added and the reaction was stirred for 10 min - 5 h (see Table 2 of the manuscript). The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~20 mL) was washed with 1% aq. NaOH (2 x 10 mL) and water (2 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-hexanes gradient elution) to afford disaccharide **5** in 9-90% yield (see Table 2 of the manuscript).

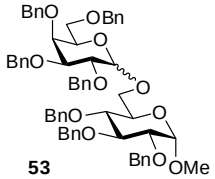
Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (51)



21

The title compound was obtained from donor **6** and acceptor **50**[24] as a white amorphous solid in 62% yield (α/β = 1/1.0). The analytical data for **7** was essentially the same as reported previously.[24]

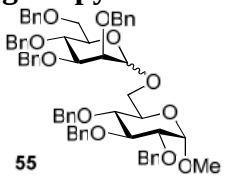
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-α-D-glucopyranoside (53)



53

The title compound was obtained from glycosyl donor **52** and acceptor **4**[24] as a white amorphous solid in 69% yield (α/β = 1/1.1). Analytical data for **53** was in accordance with that reported previously.[26,35]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-α-D-glucopyranoside (55)

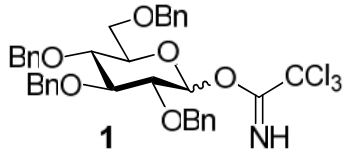


55

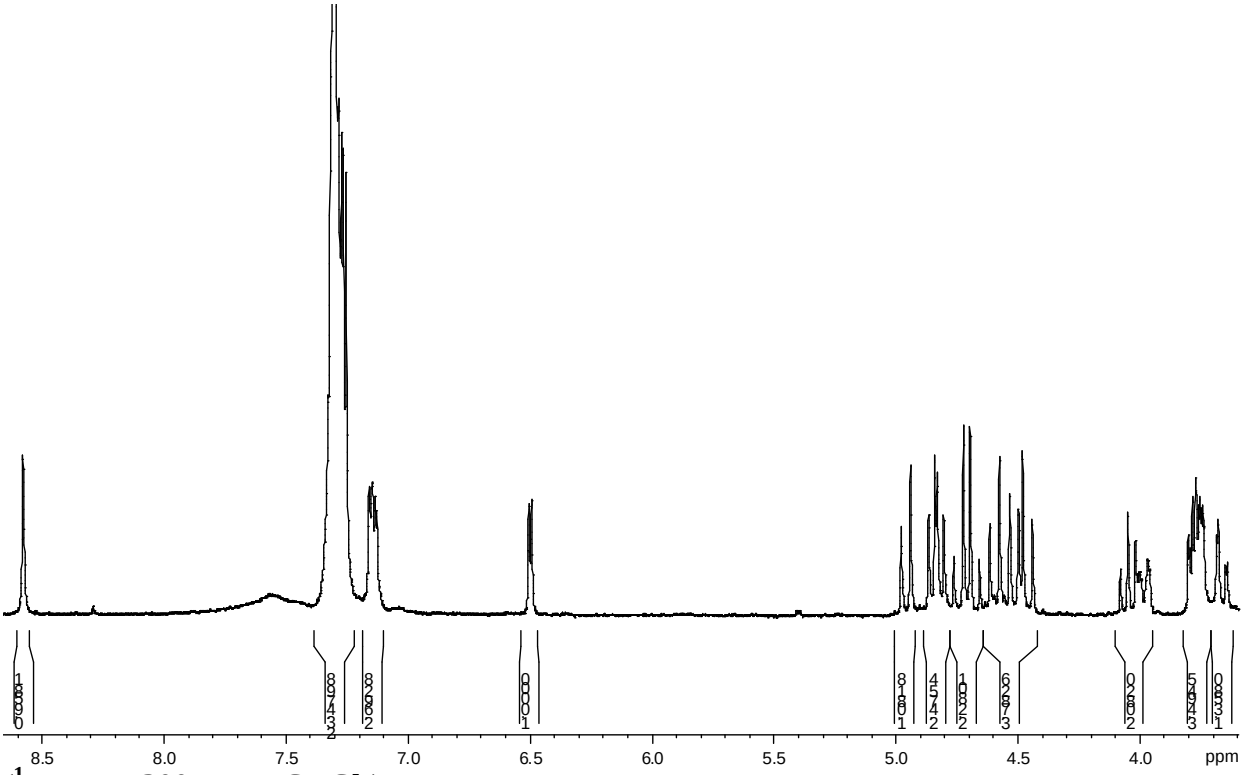
The title compound was obtained from donor **54** and acceptor **4** as a white amorphous solid in 75% yield (α/β = 2.5/1). The title compound was reported previously.[36]

NMR spectra

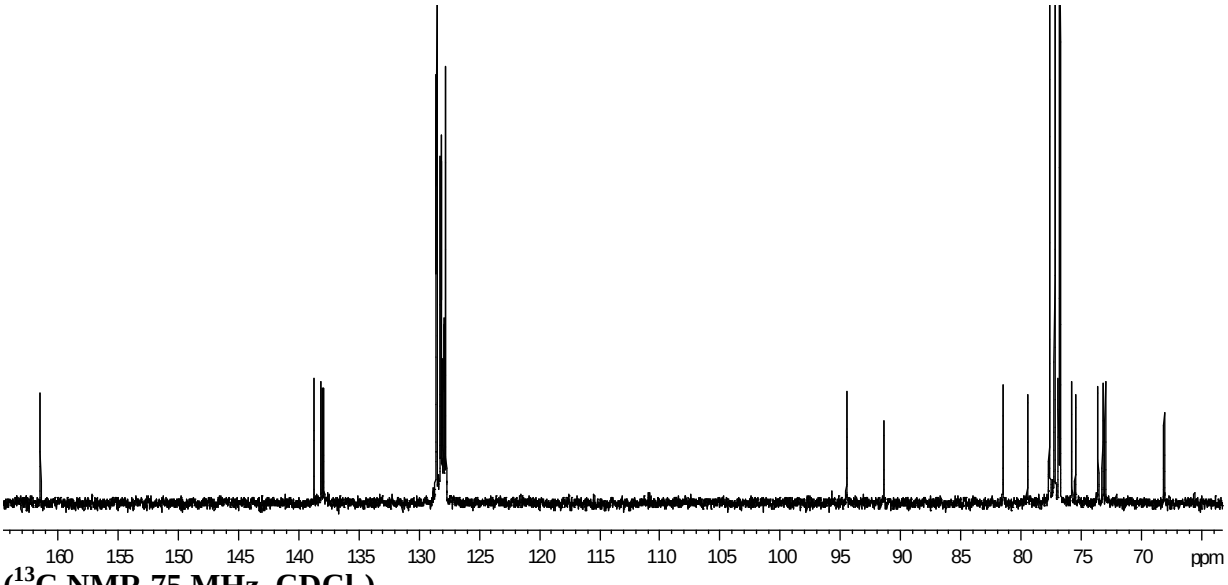
2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl trichloroacetimidate (1)



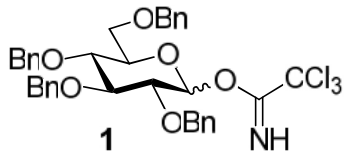
1



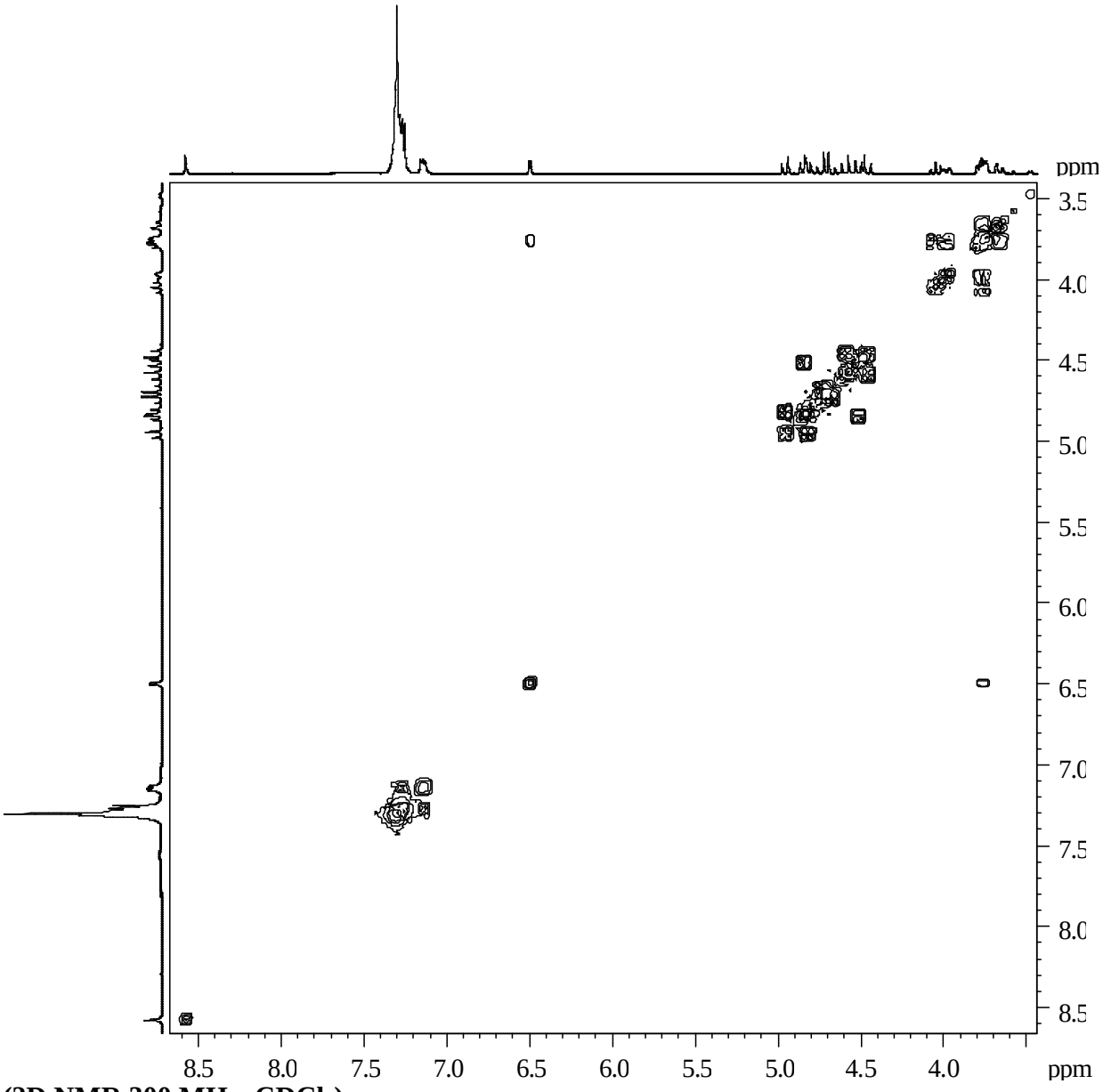
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)

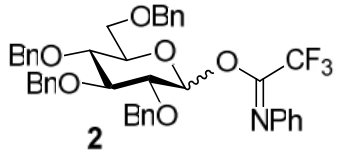


1

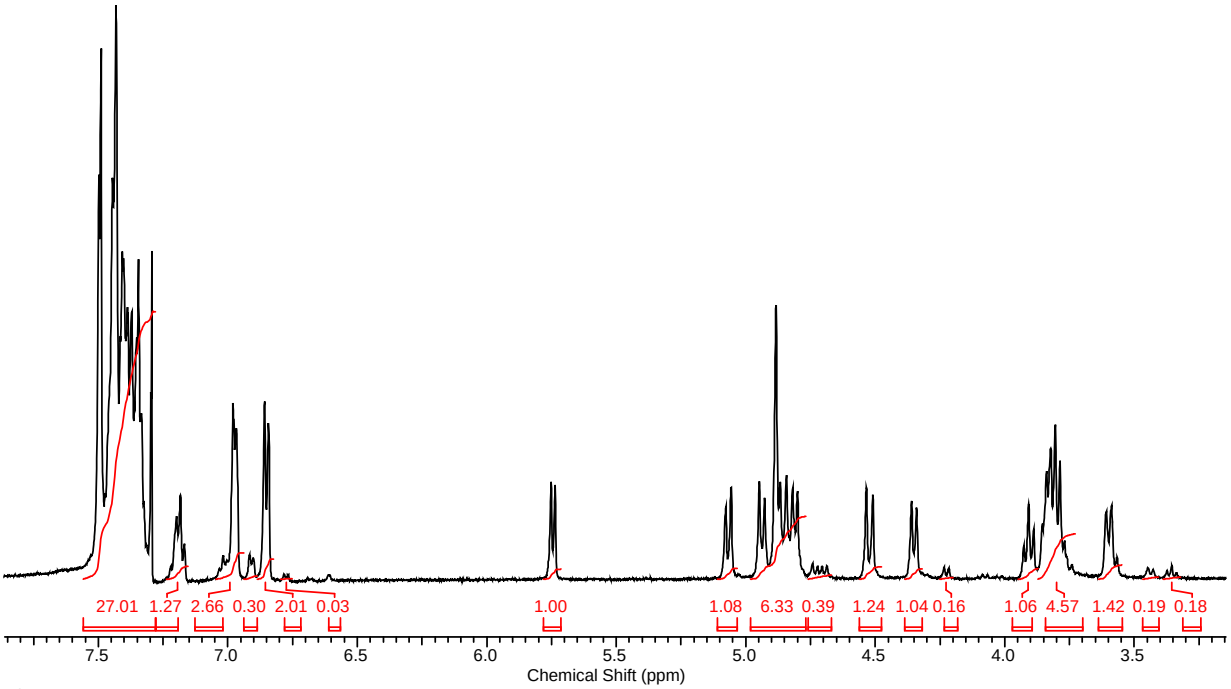


(2D NMR 300 MHz, $CDCl_3$)

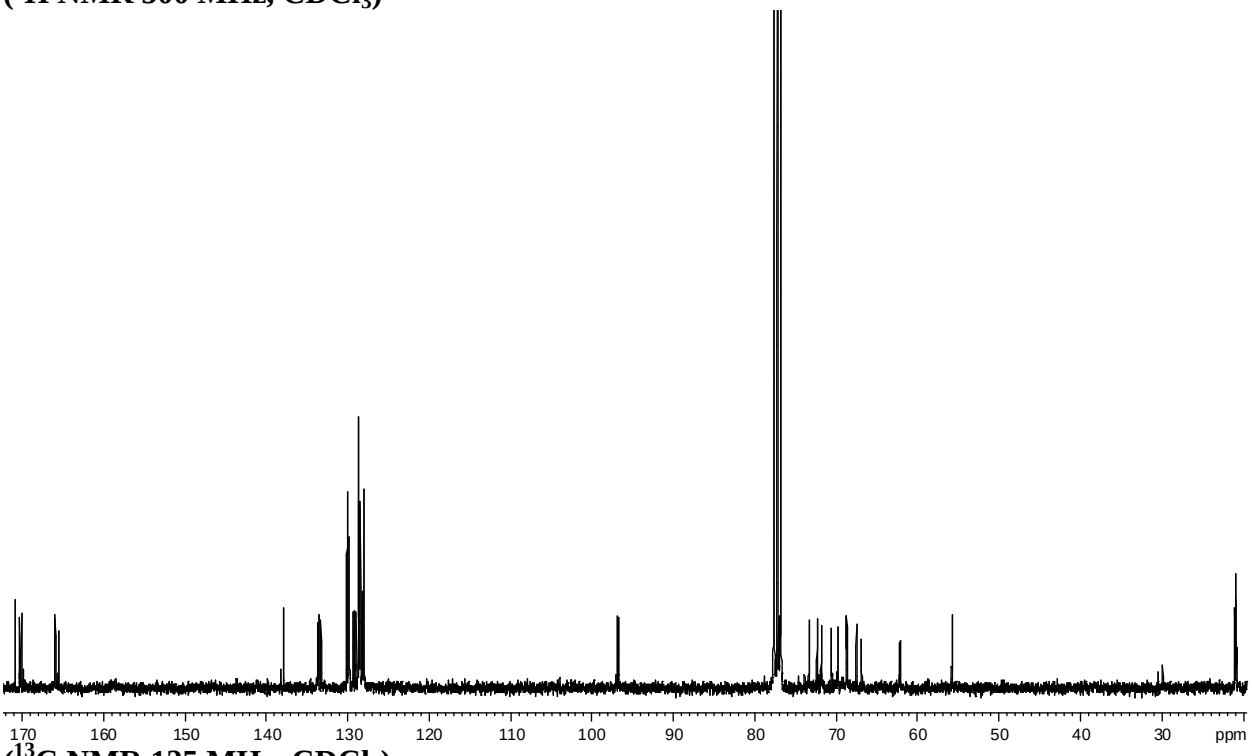
2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl N-phenyltrifluoroacetimidate (2)



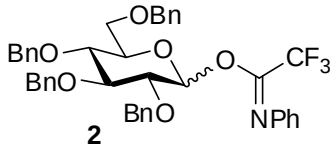
2



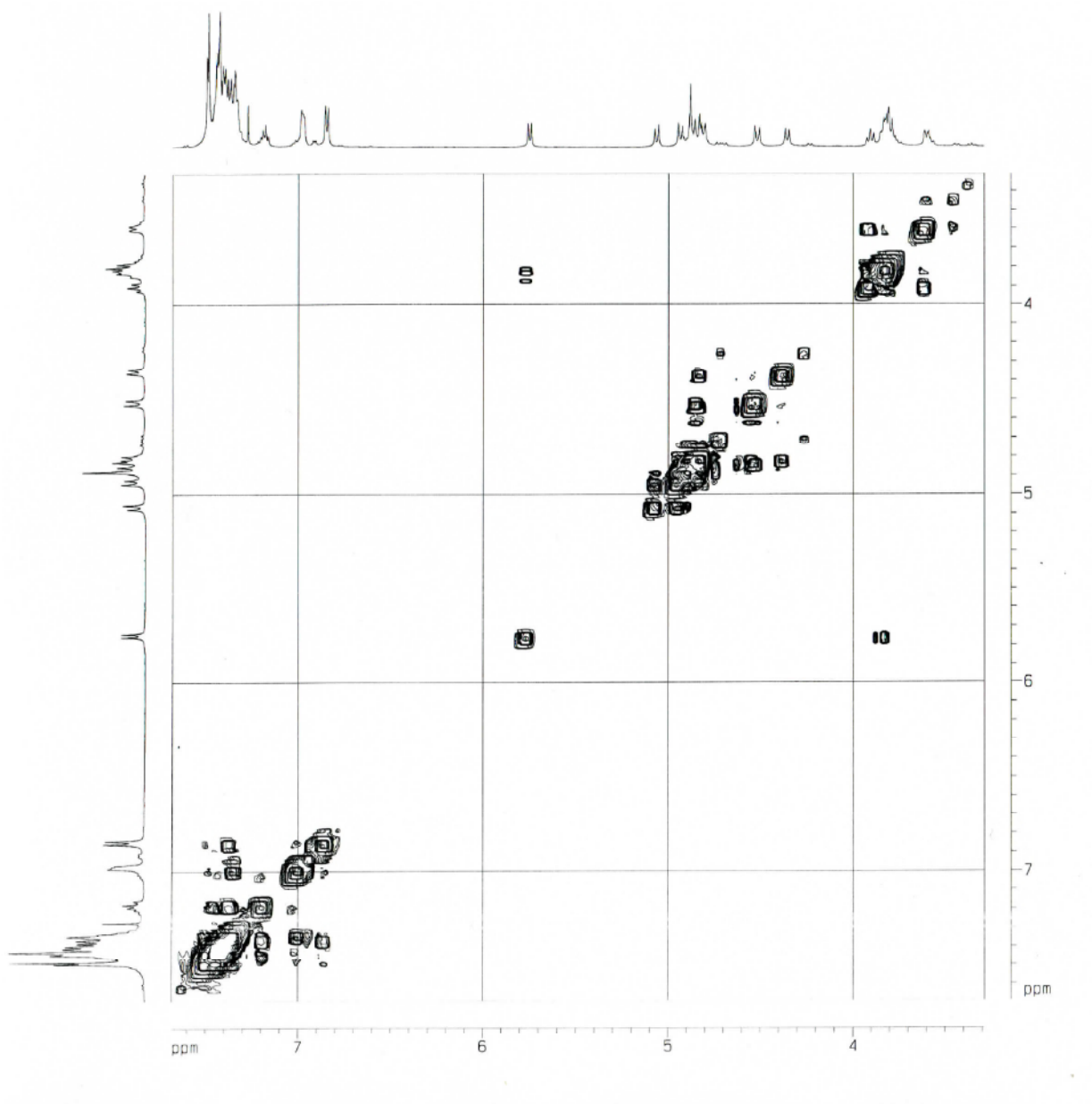
(^{1}H NMR 500 MHz, $CDCl_3$)



(^{13}C NMR 125 MHz, $CDCl_3$)

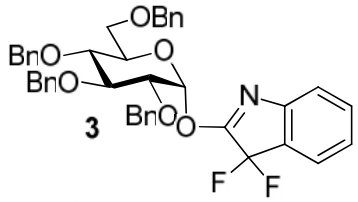


2

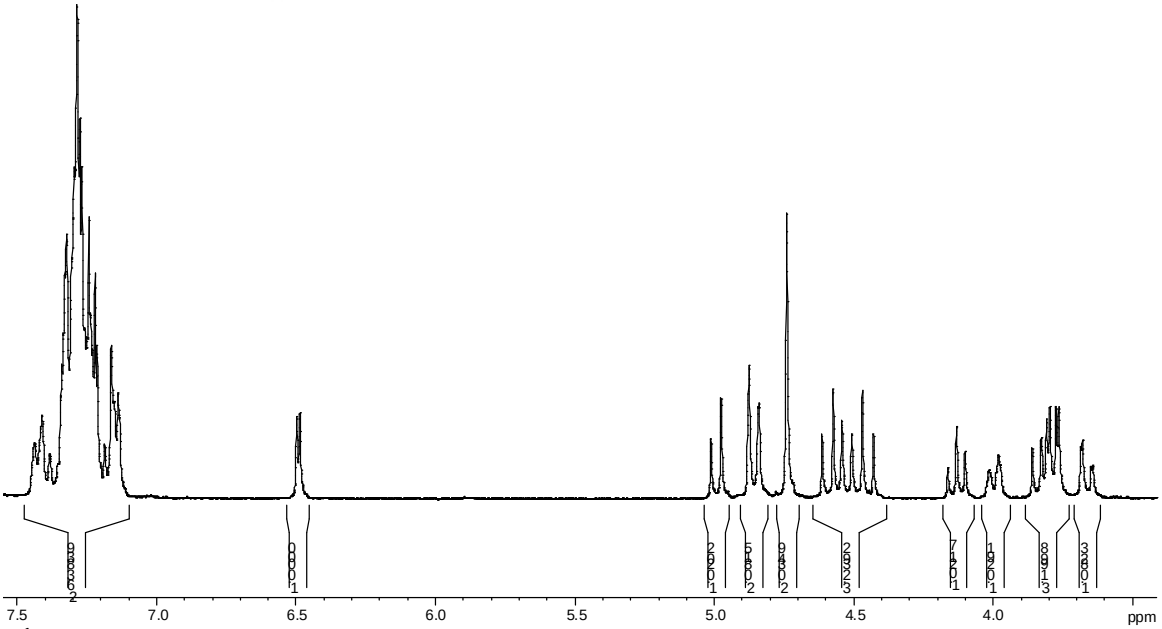


(2D NMR 500 MHz, $CDCl_3$)

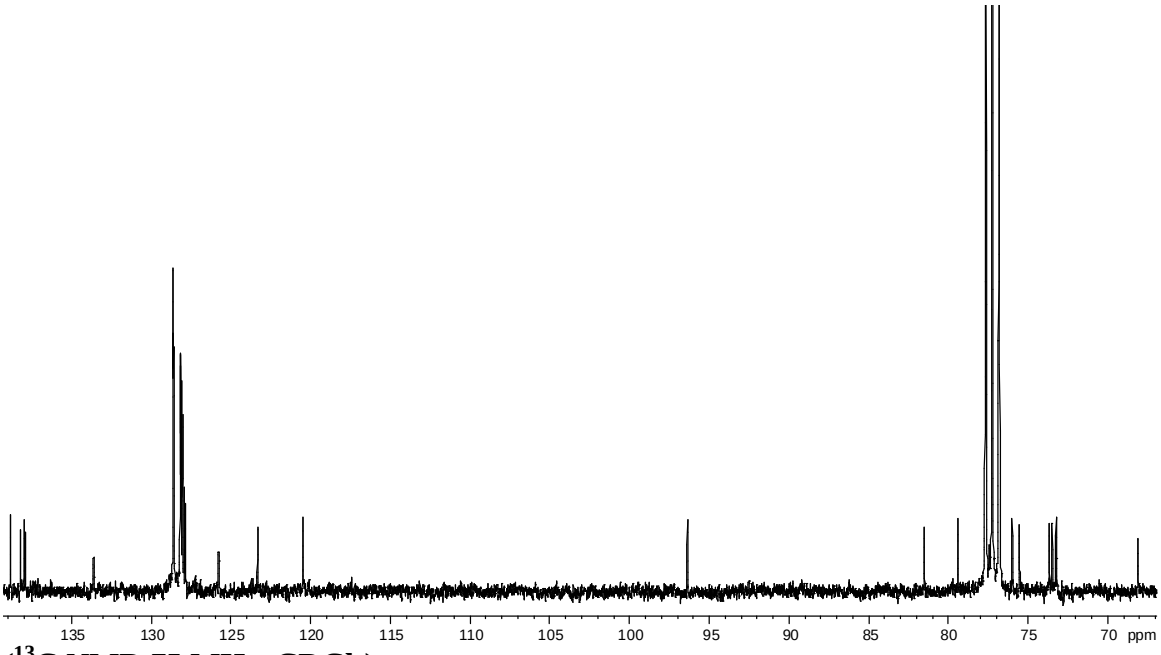
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (3)



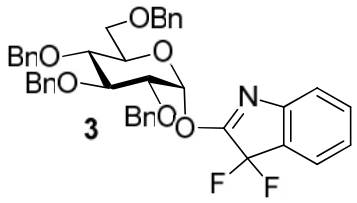
3

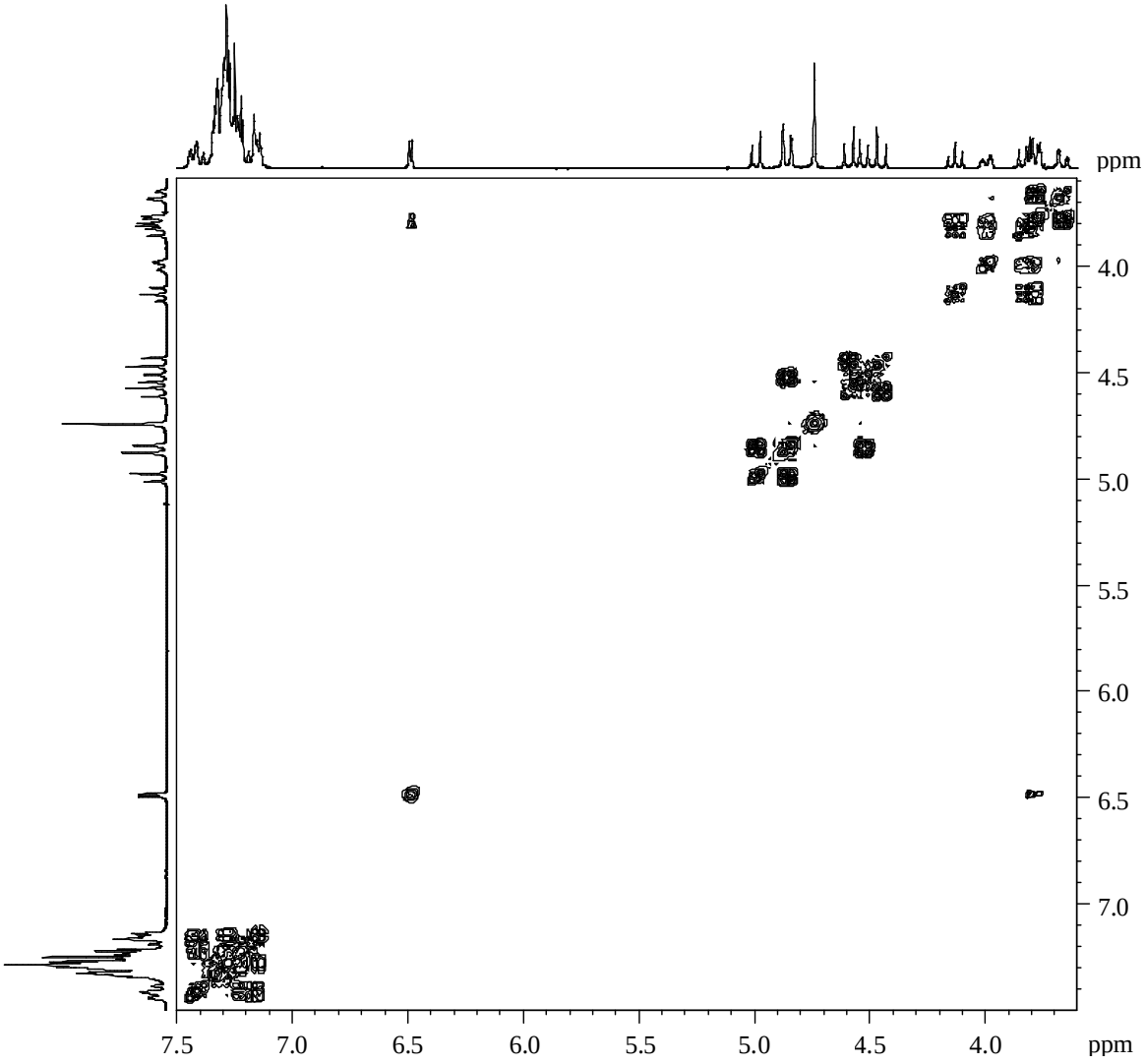


(^{1}H NMR 300 MHz, $CDCl_3$)



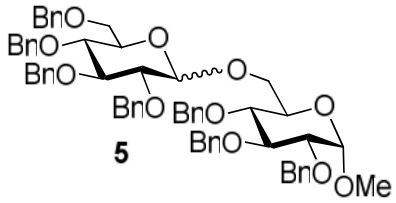
(^{13}C NMR 75 MHz, $CDCl_3$)



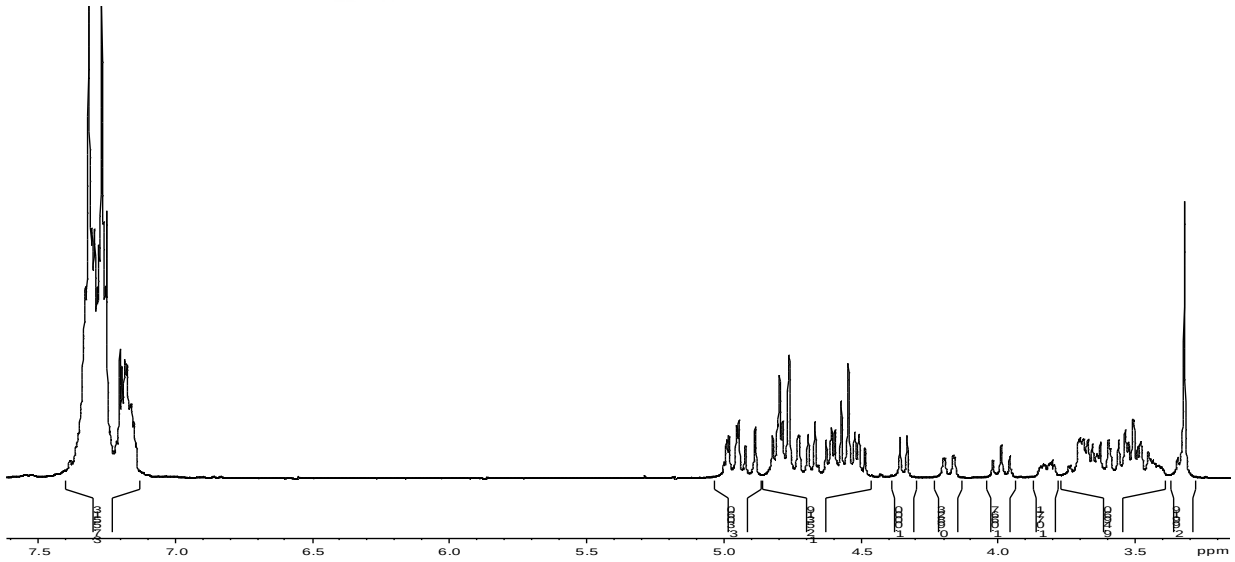


(2D NMR 300 MHz, $CDCl_3$)

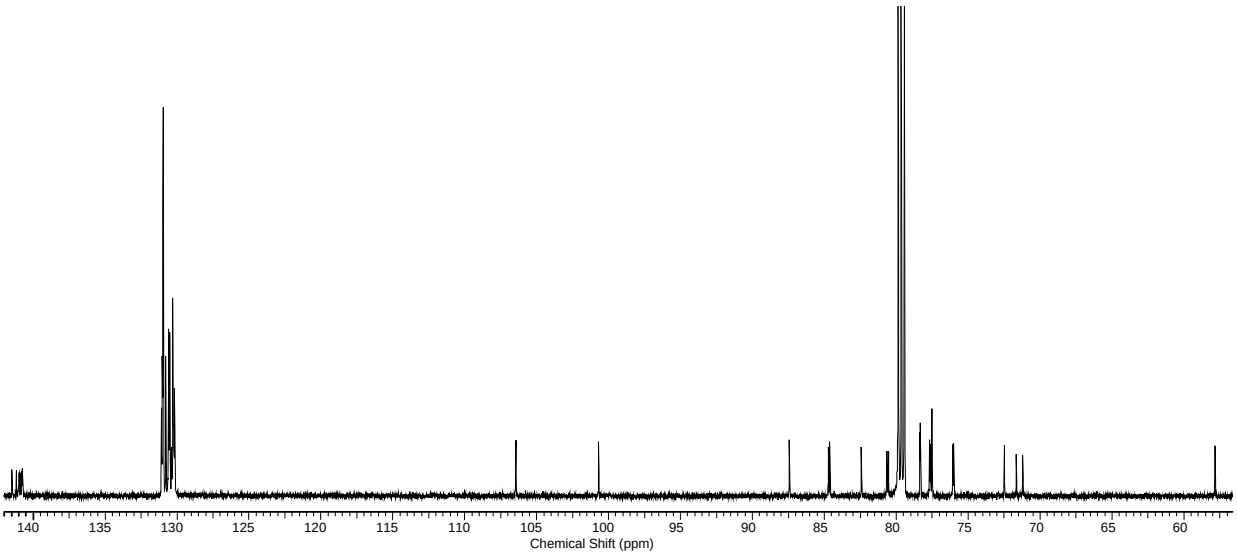
Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (5)



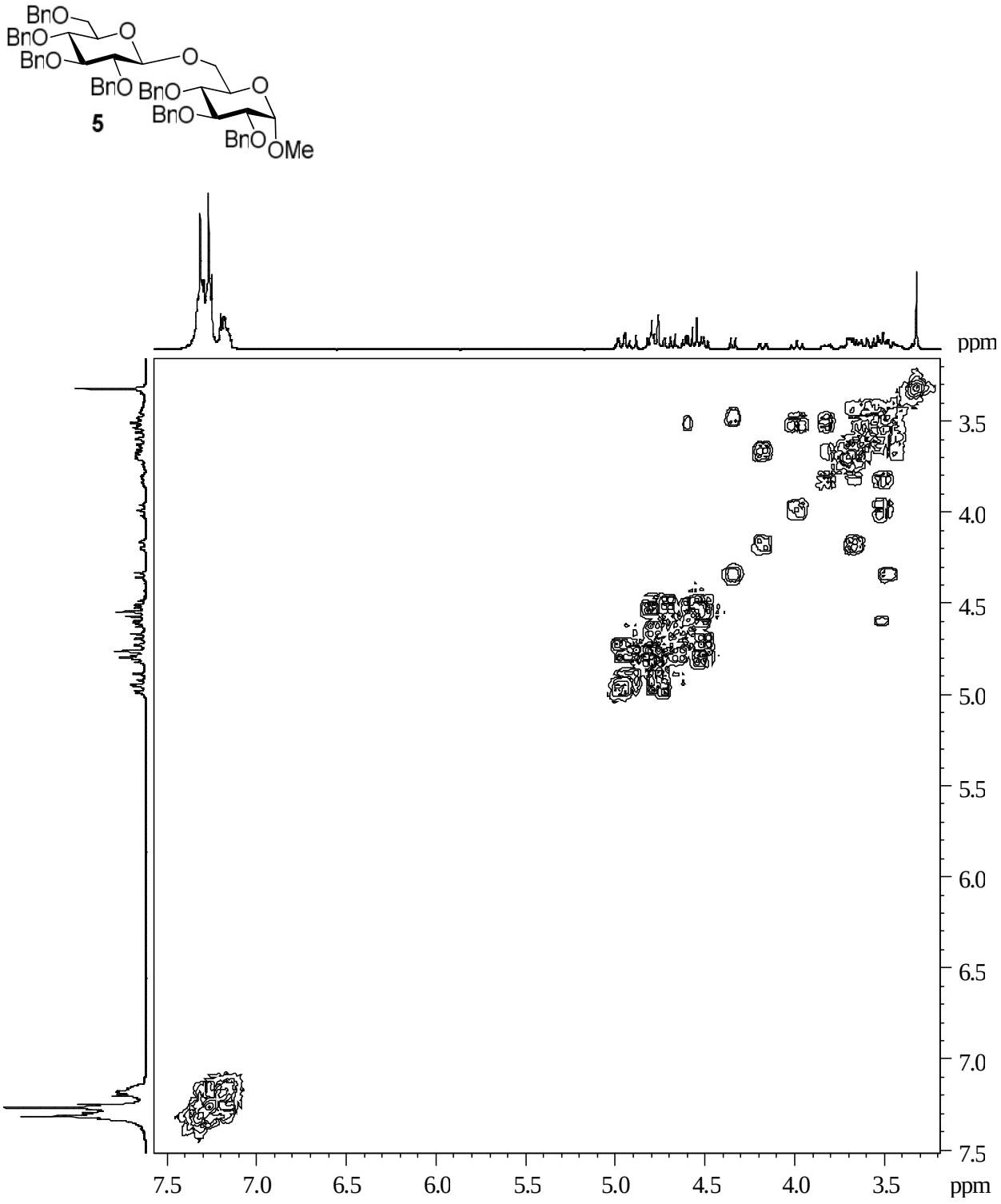
5



(^{1}H NMR 300 MHz, $CDCl_3$)

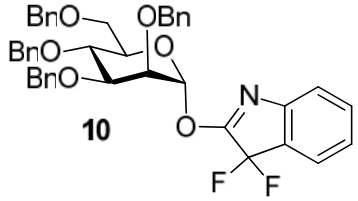


(^{13}C NMR 150 MHz, $CDCl_3$)

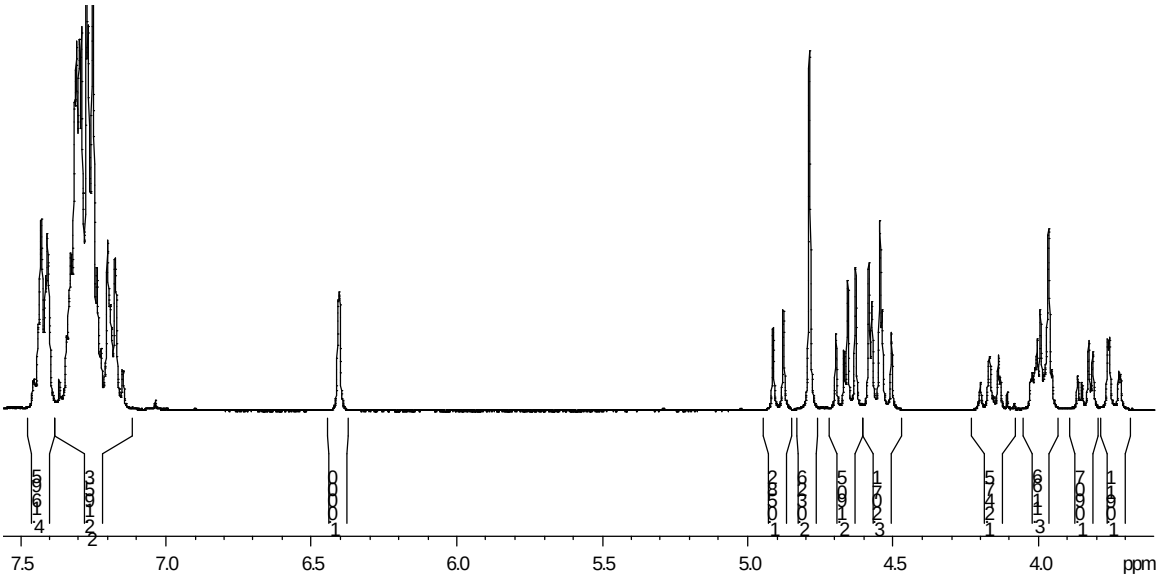


(2D NMR 300 MHz, $CDCl_3$)

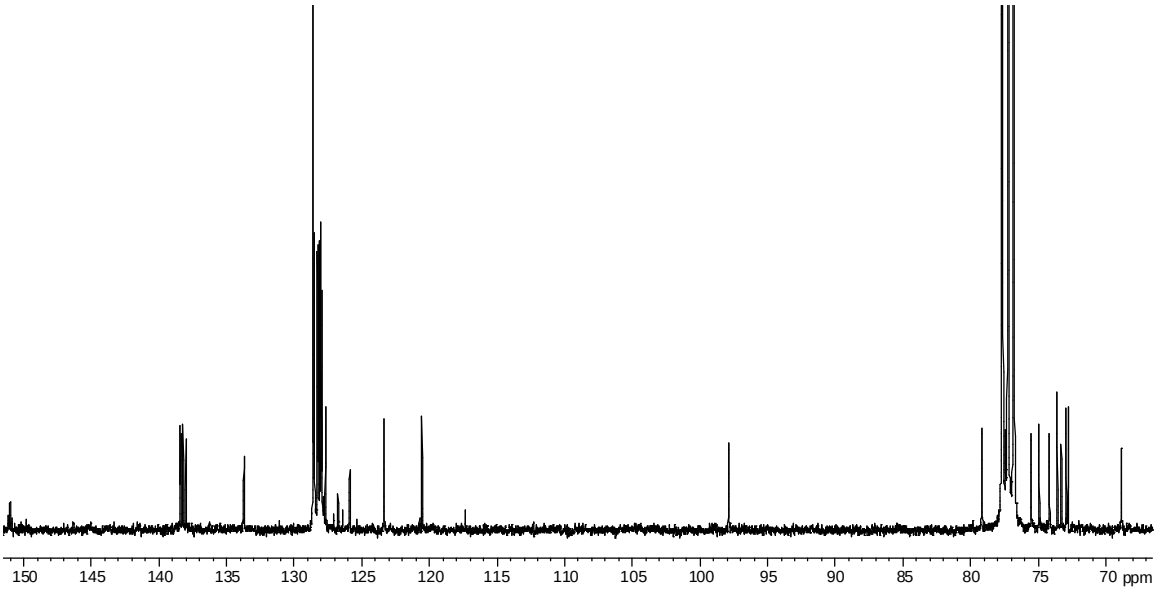
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (10)



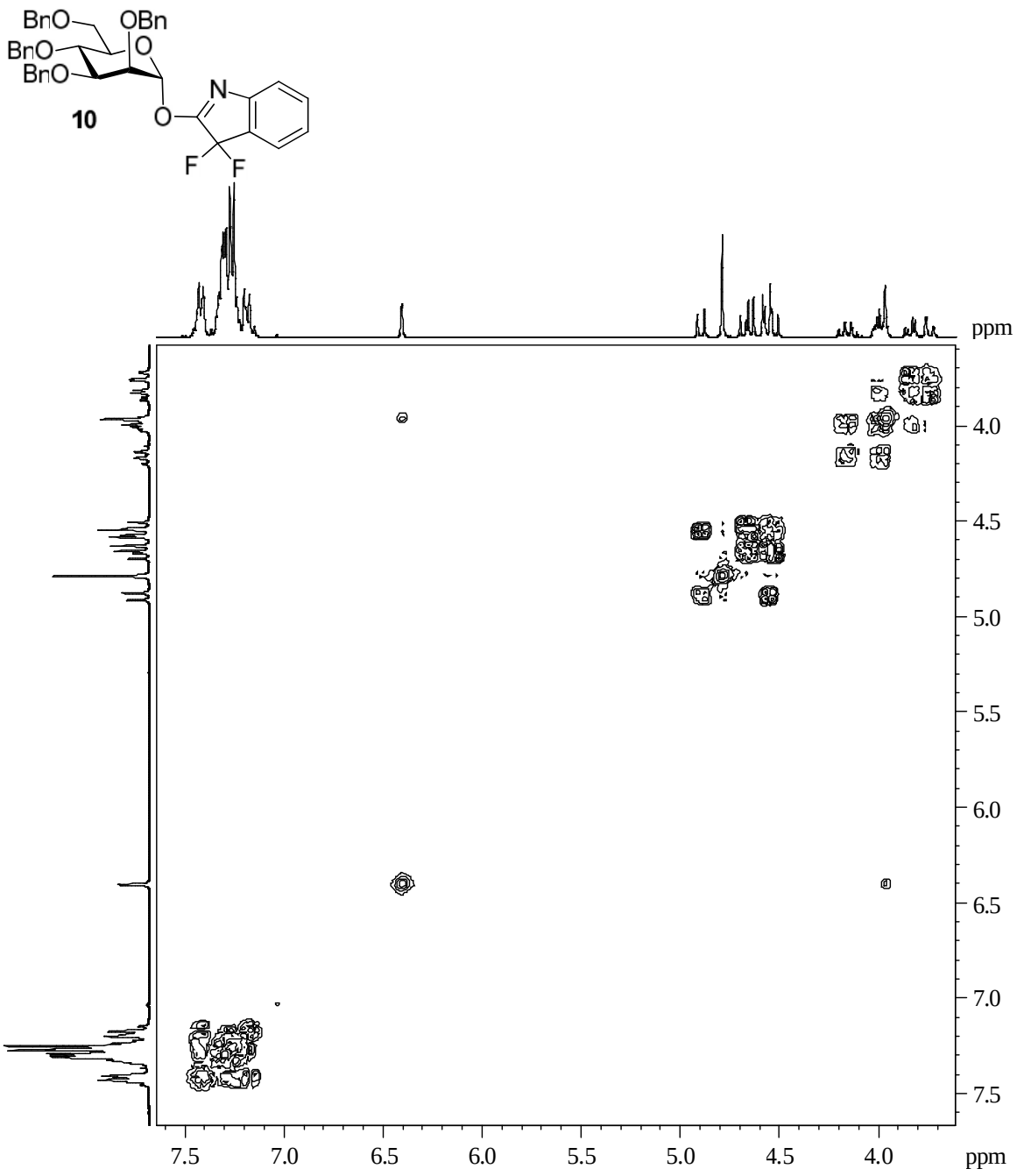
10



(^{1}H NMR 300 MHz, $CDCl_3$)

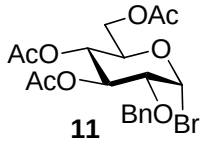


(^{13}C NMR 75 MHz, $CDCl_3$)

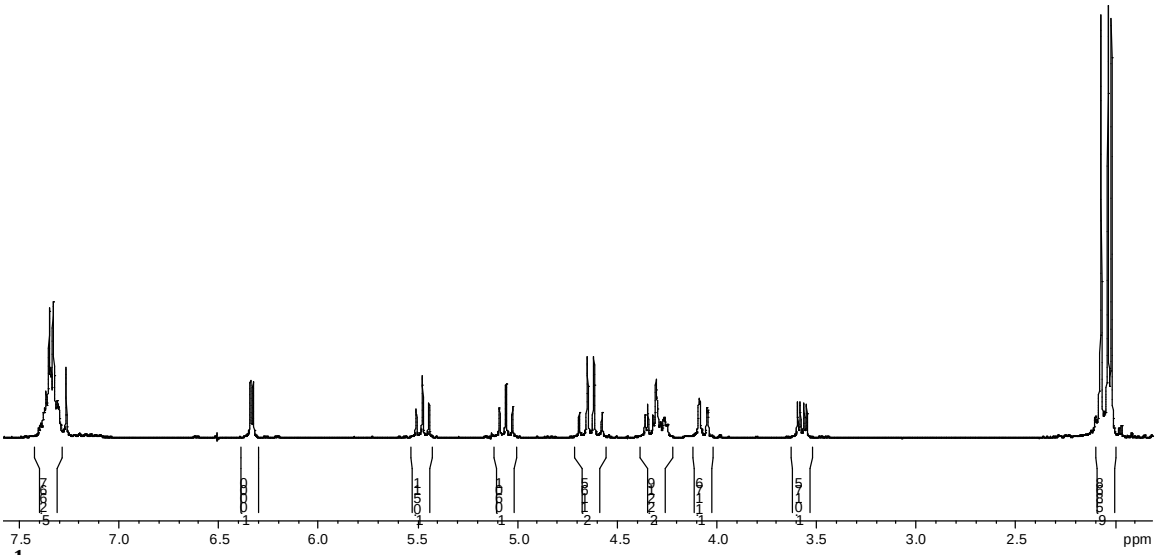


(2D NMR 300 MHz, $CDCl_3$)

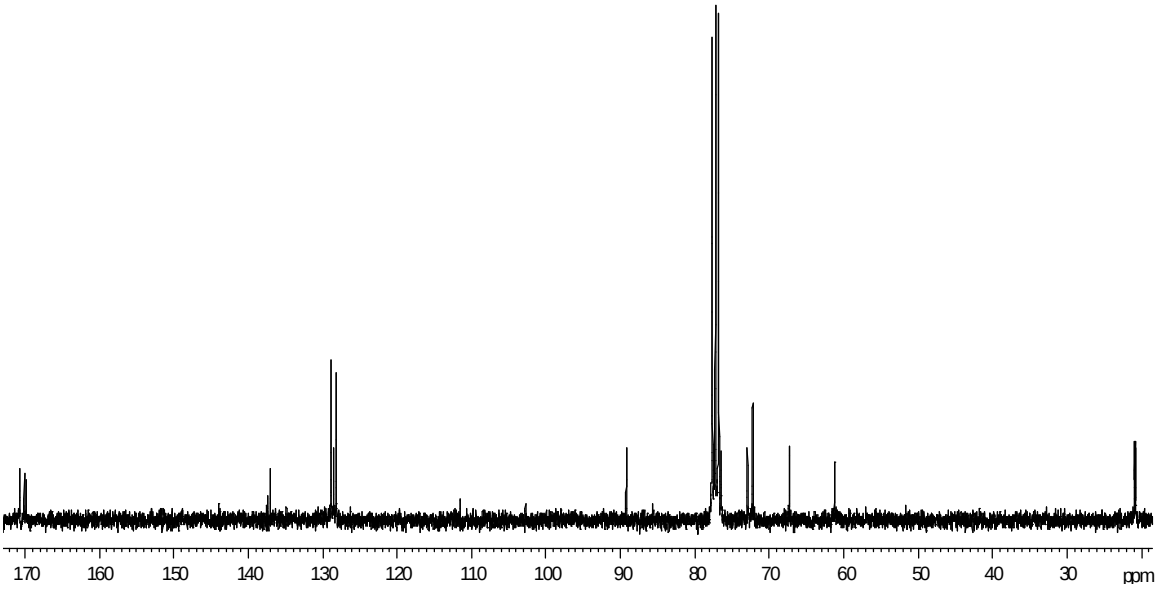
3,4,6-Tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl bromide (11)



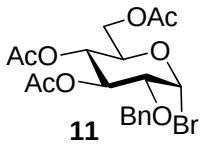
11



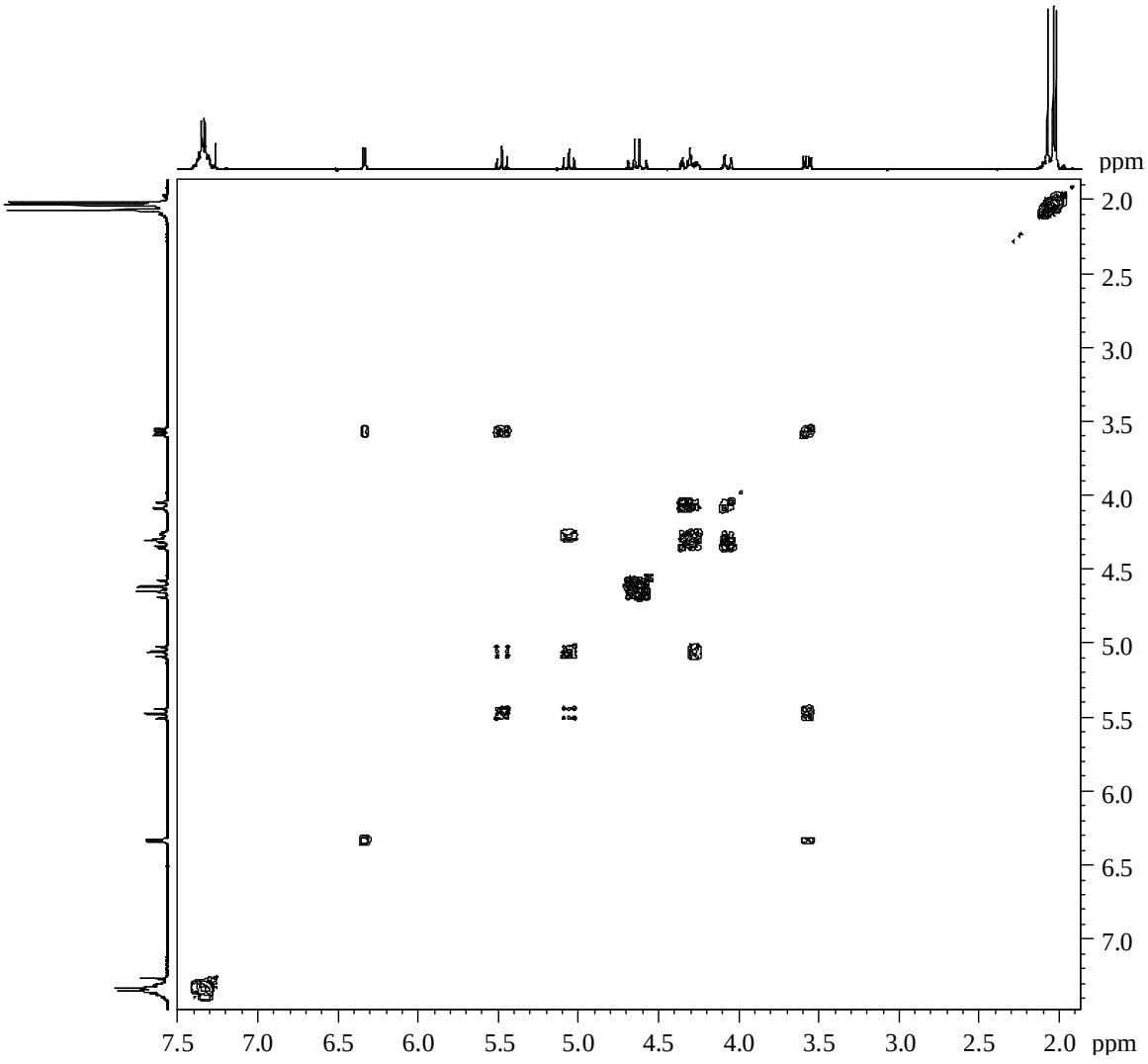
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)

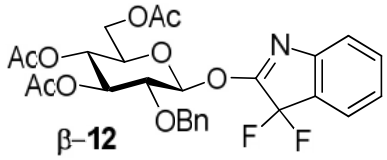


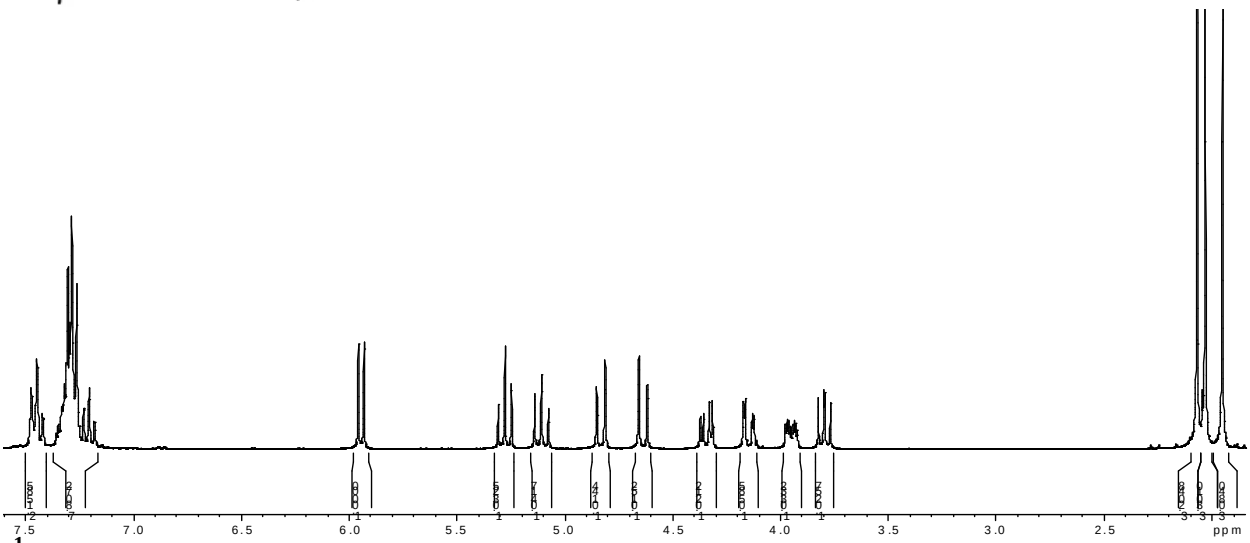
11



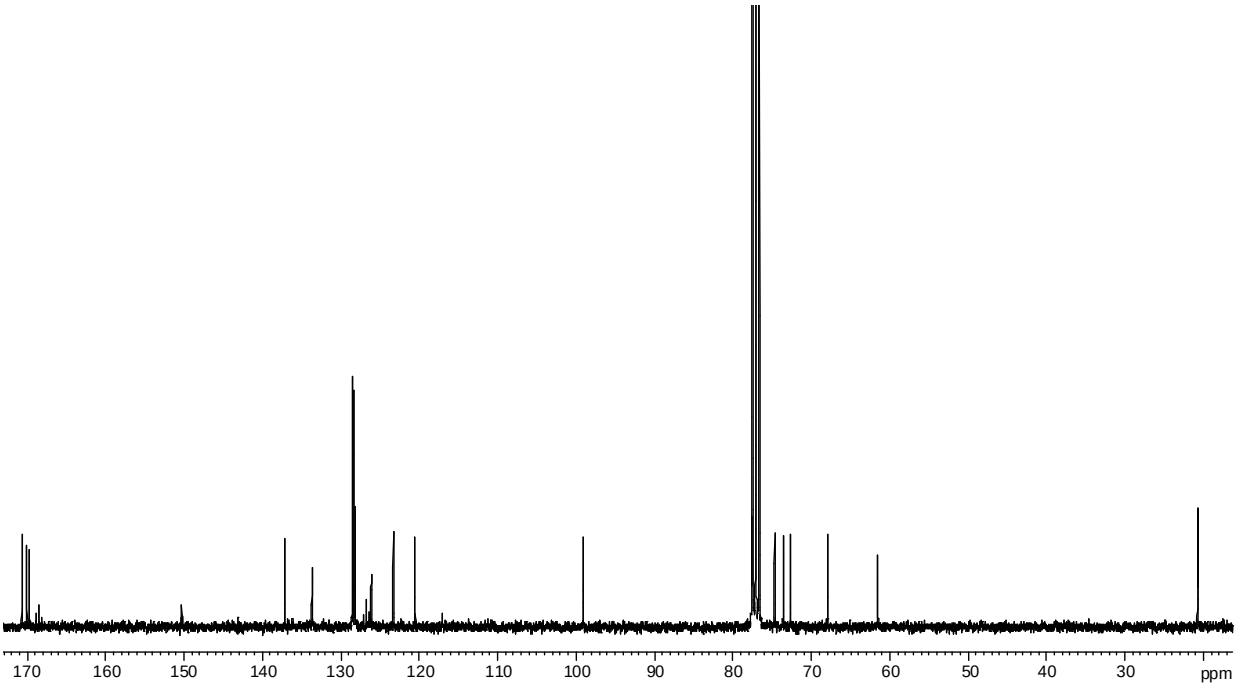
(2D NMR 300 MHz, $CDCl_3$)

3,3-Difluoro-3*H*-indol-2-yl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-β-D-glucopyranoside (β-12)

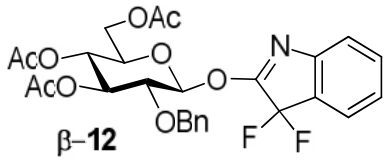




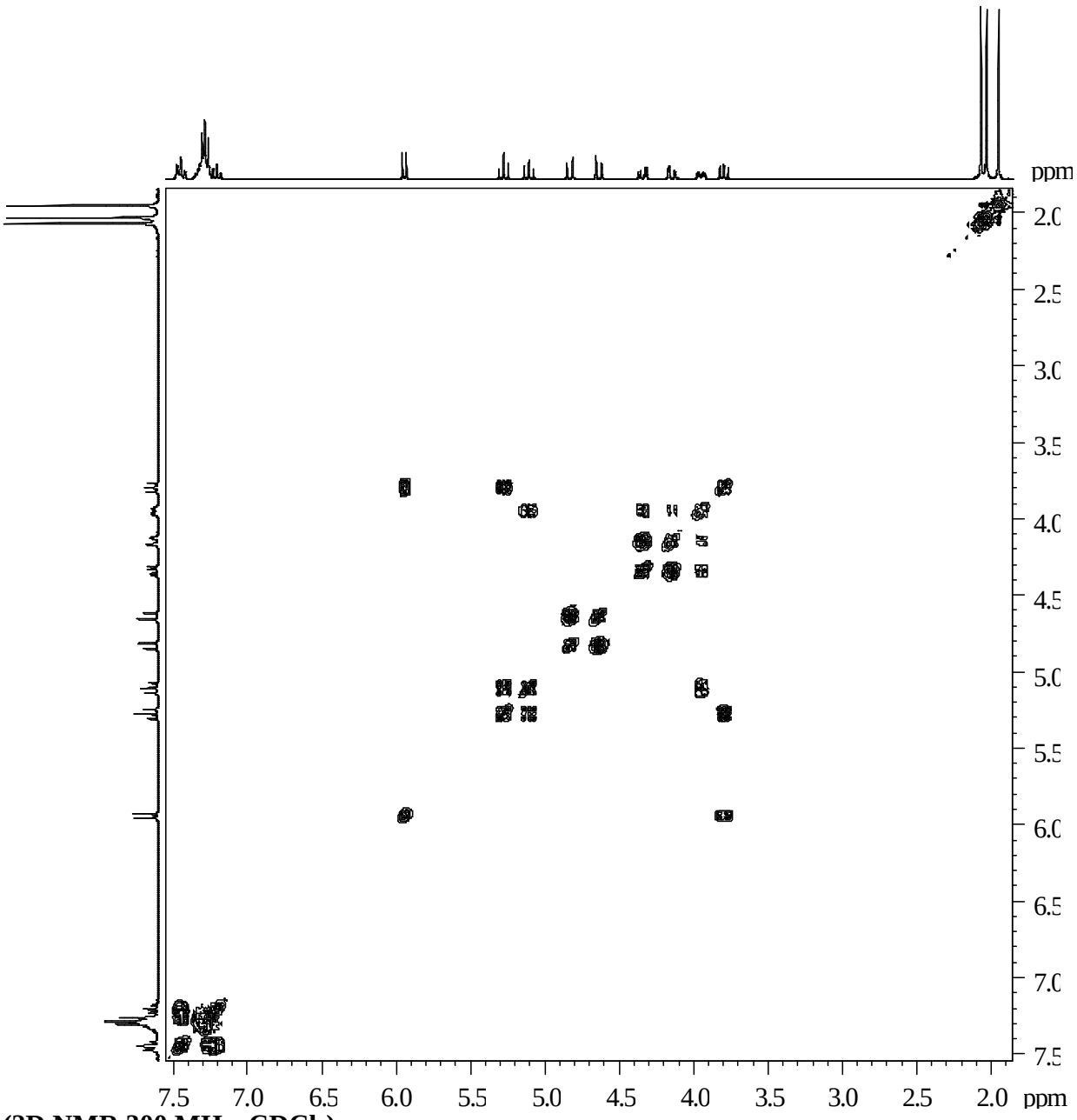
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)

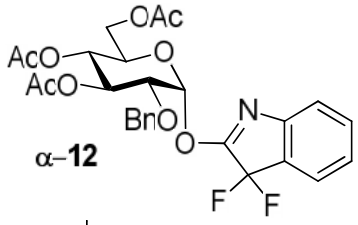


β–**12**

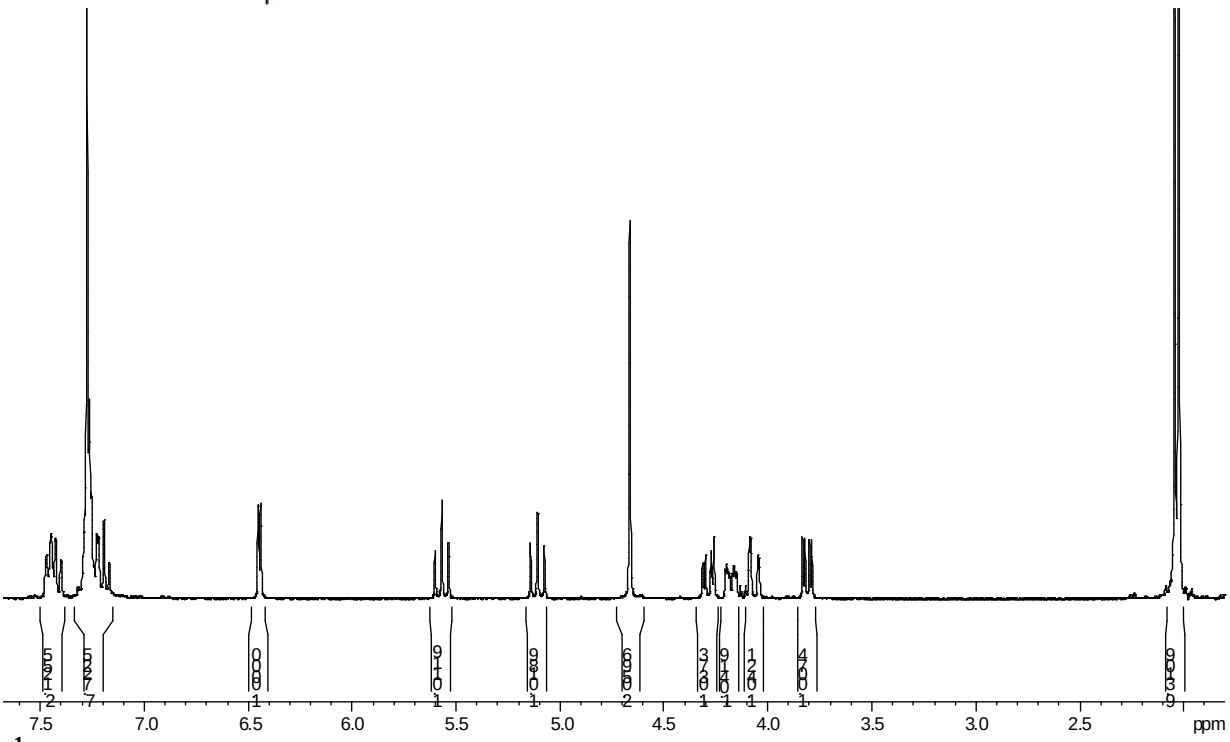


(2D NMR 300 MHz, $CDCl_3$)

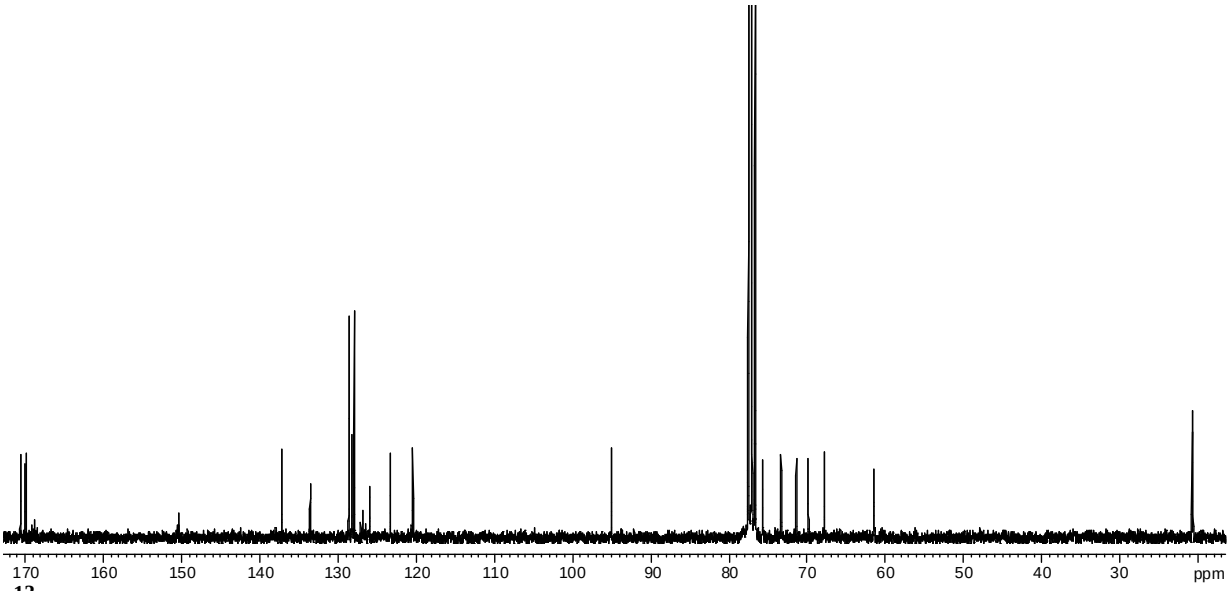
3,3-Difluoro-3*H*-indol-2-yl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranoside (α-12)



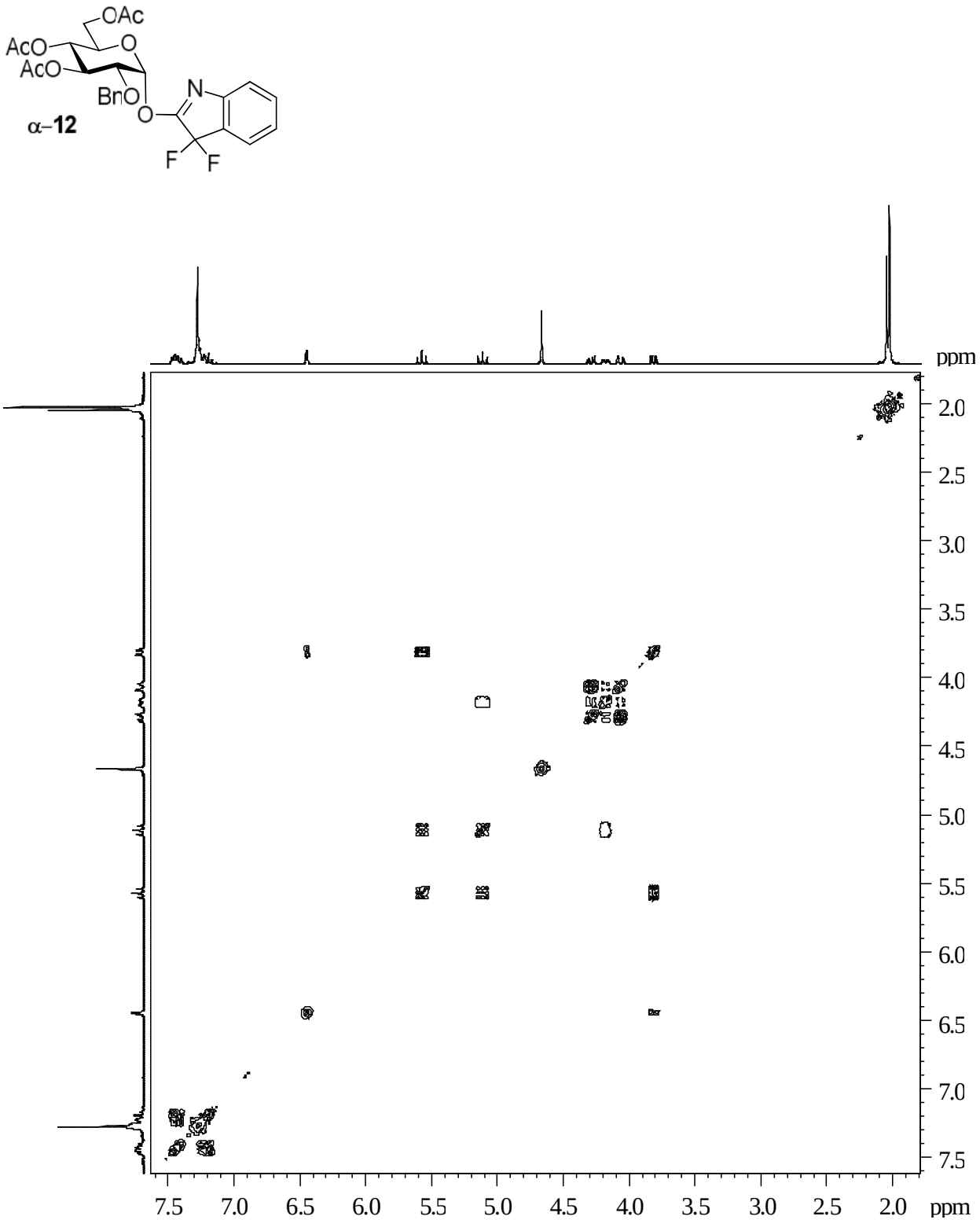
α–**12**



(**^{1}H NMR 300 MHz, $CDCl_3$**)

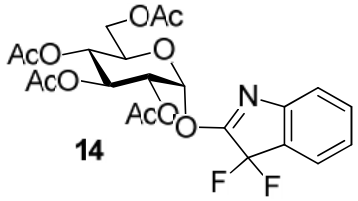


(**^{13}C NMR 75 MHz, $CDCl_3$**)

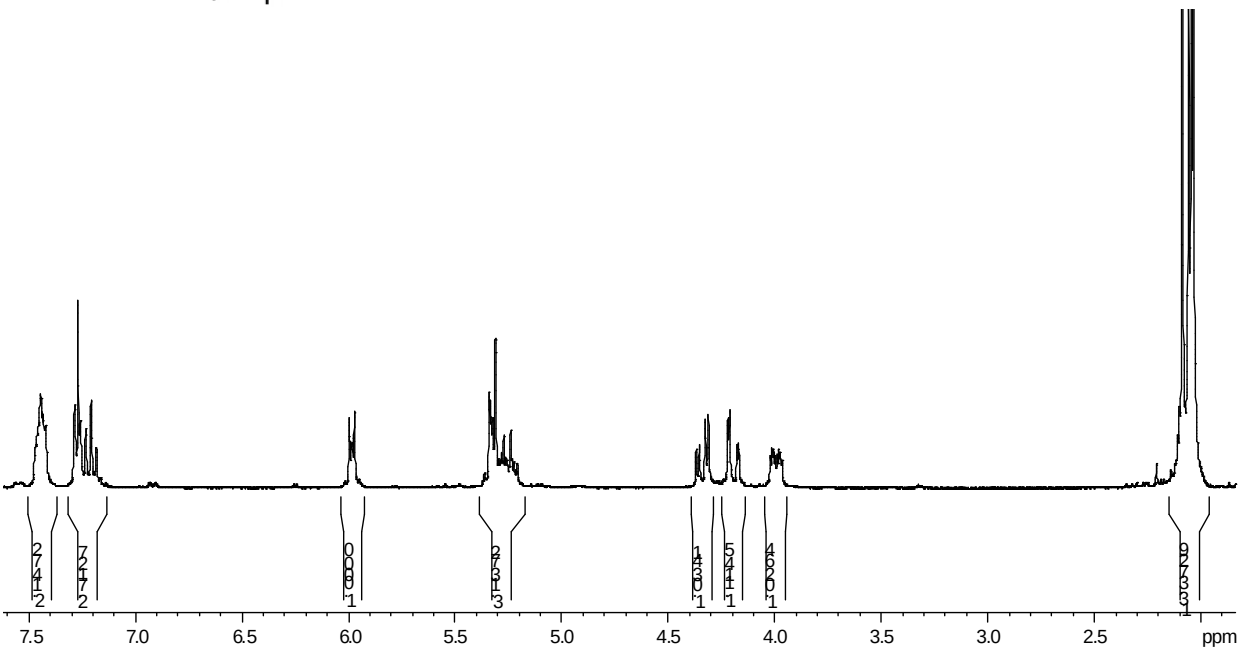


(2D NMR 300 MHz, $CDCl_3$)

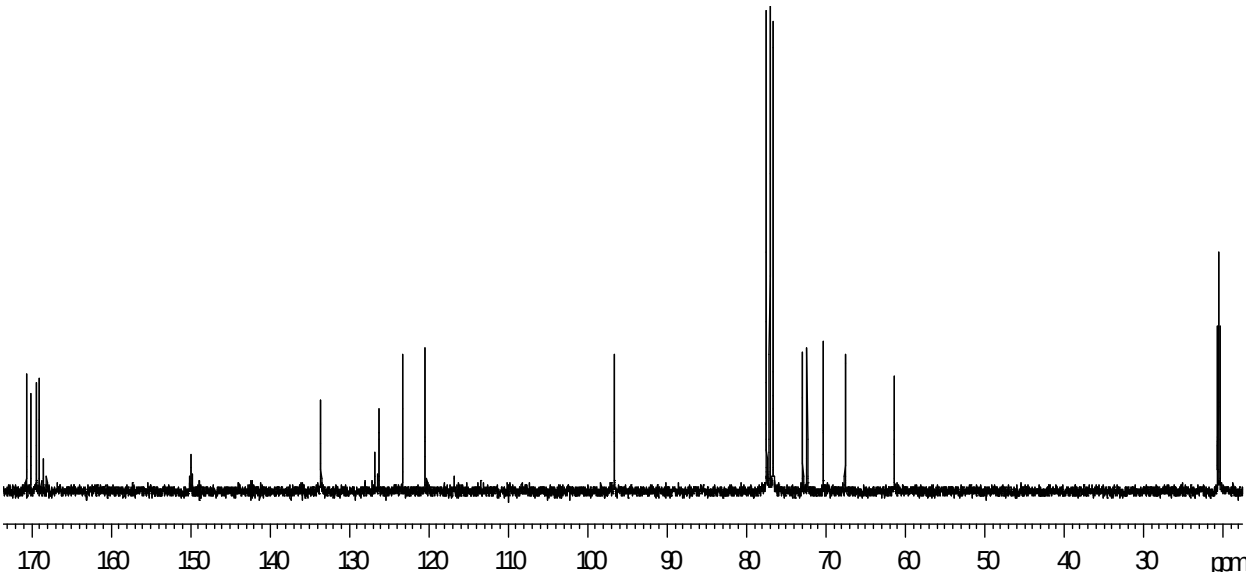
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (14)



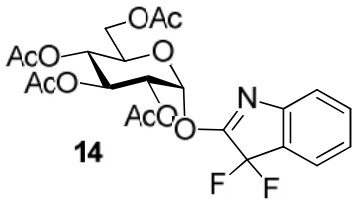
14



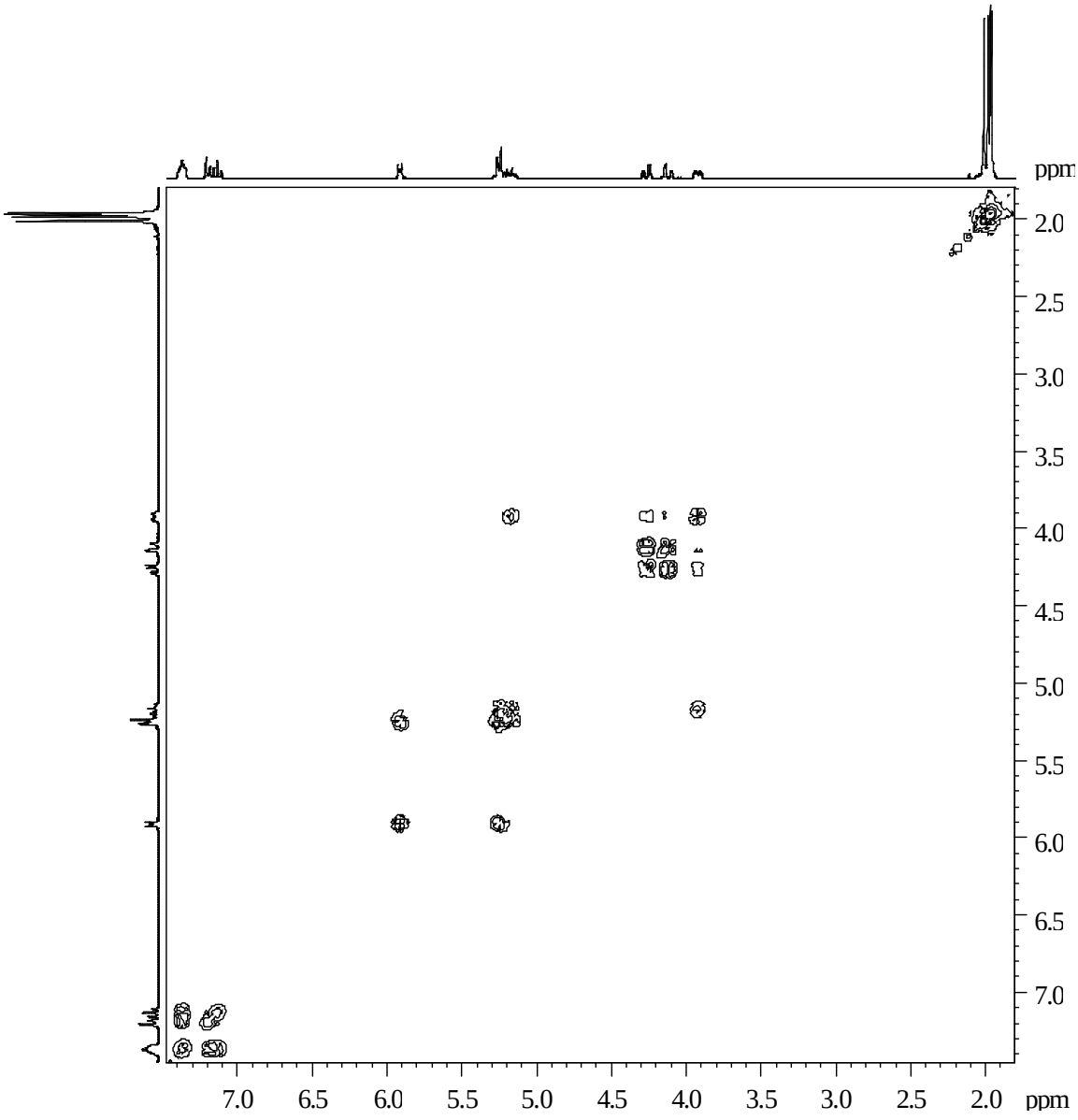
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)

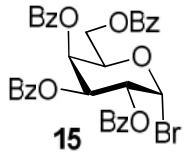


14

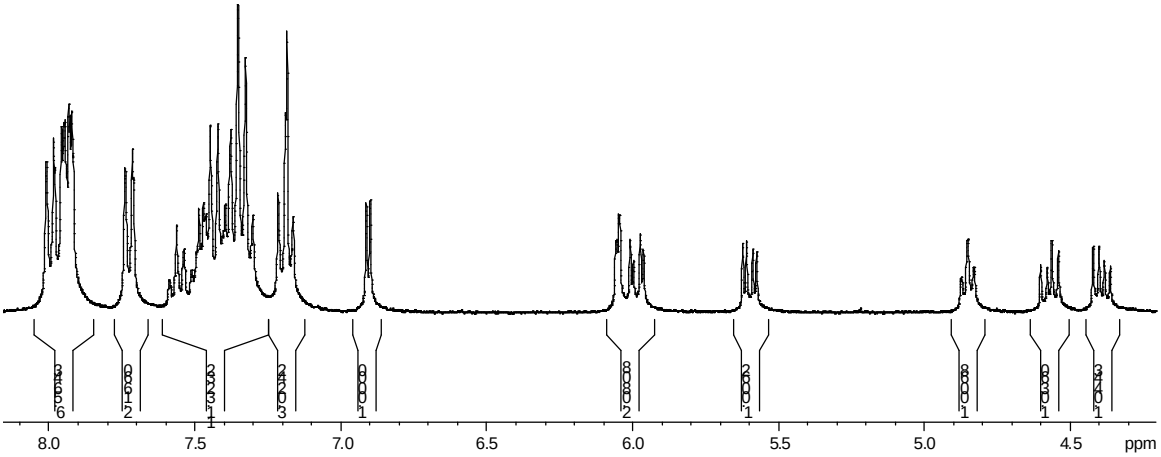


(2D NMR 300 MHz, $CDCl_3$)

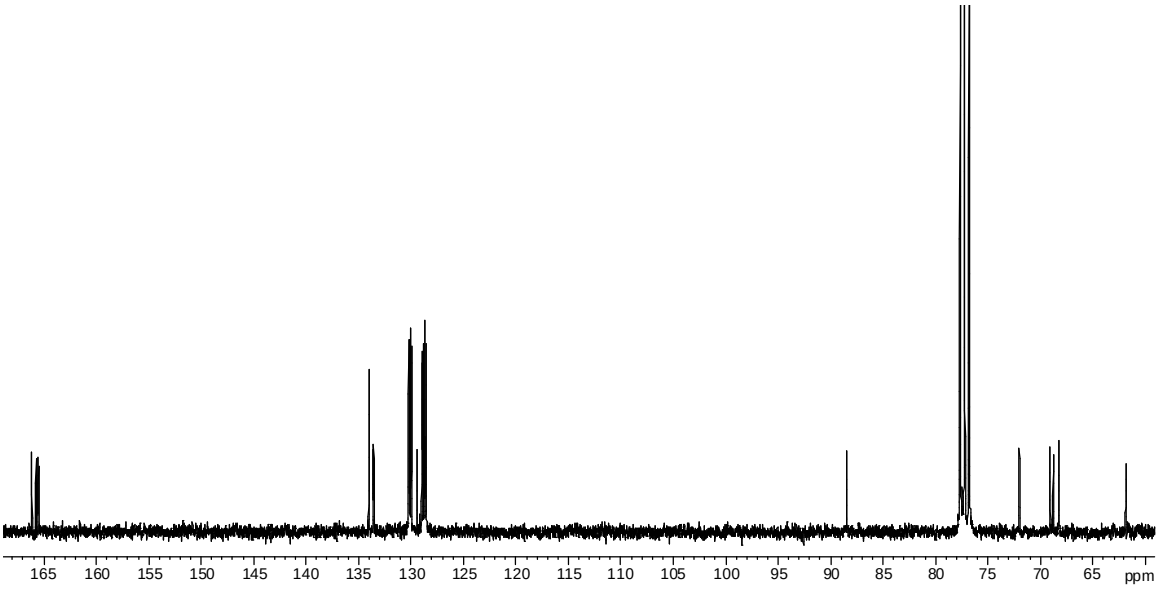
2,3,4,6-Tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (15)



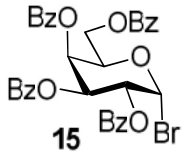
15



(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)



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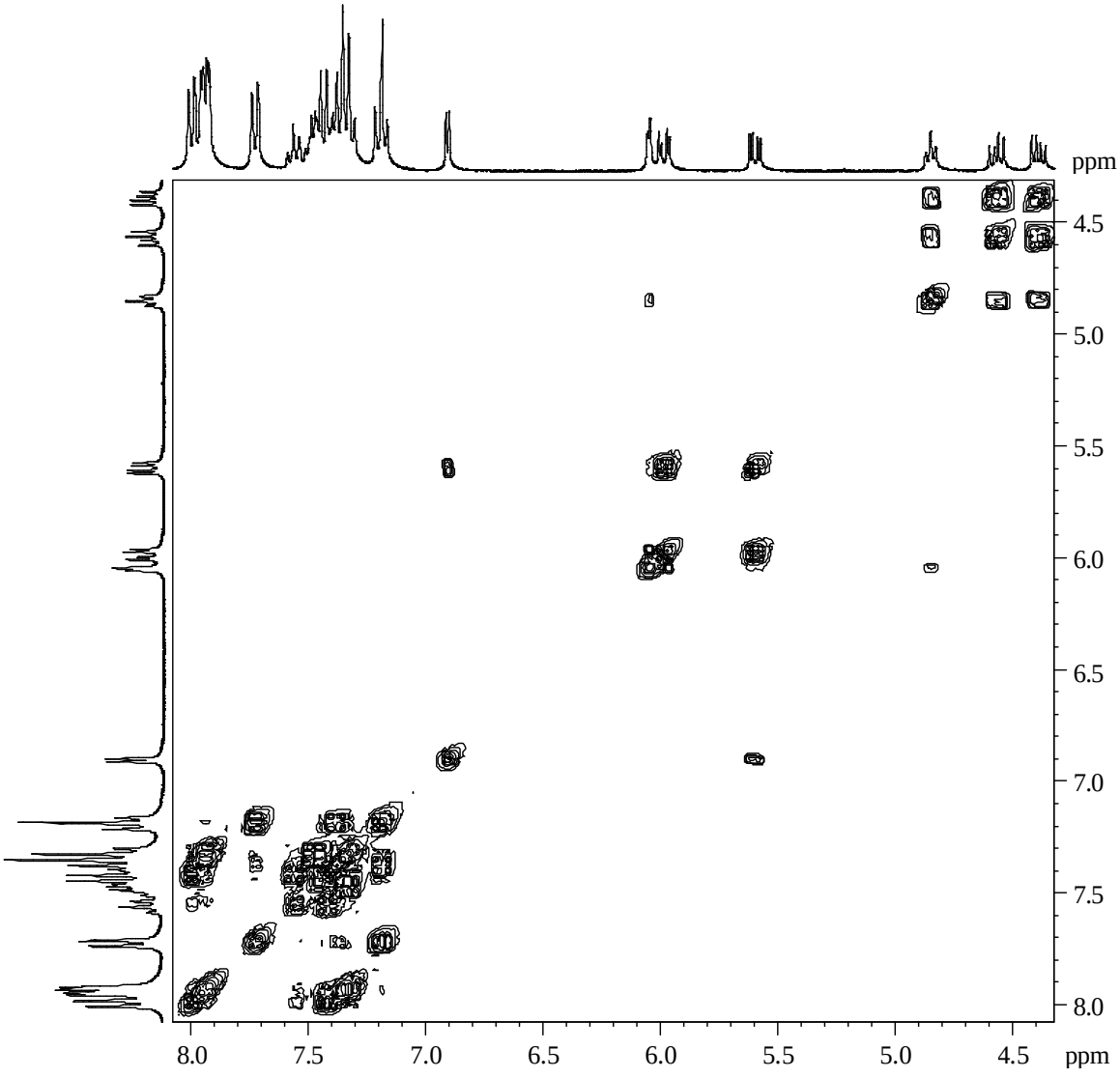
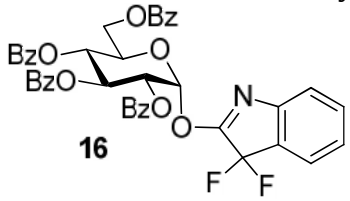
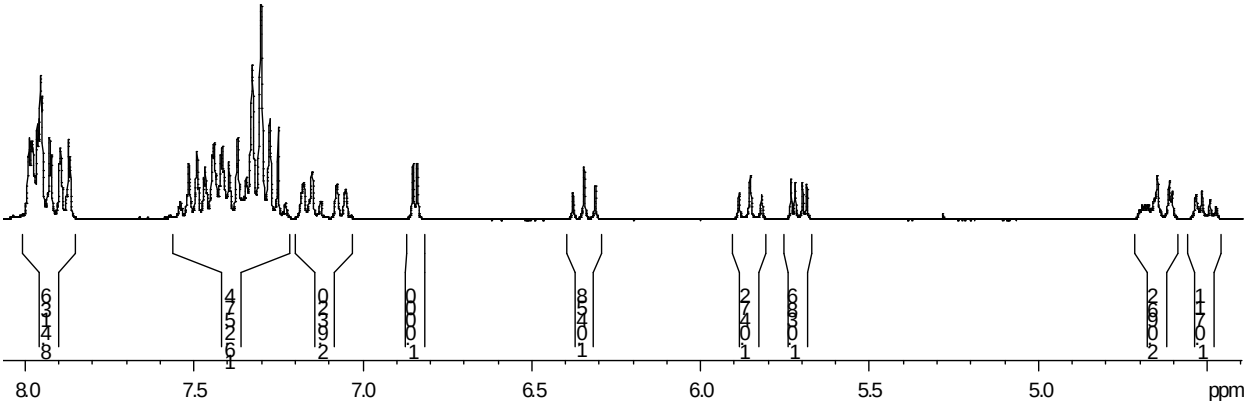


(2D NMR 300 MHz, $CDCl_3$)

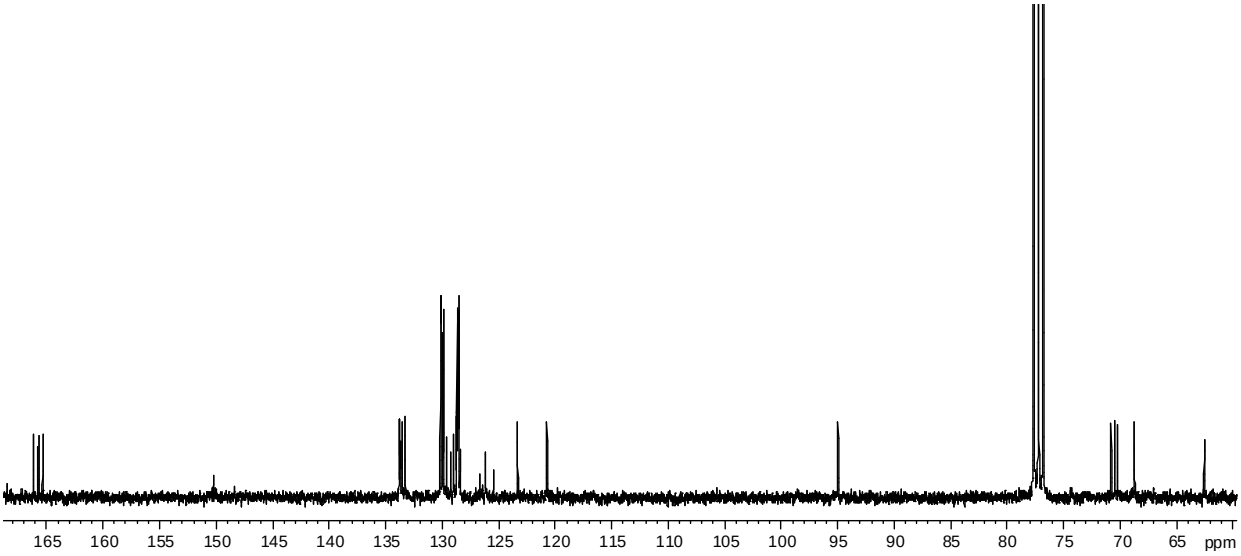
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranoside (16)



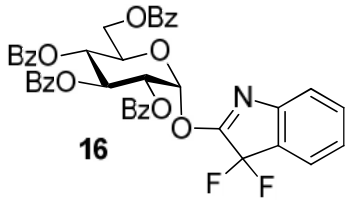
16



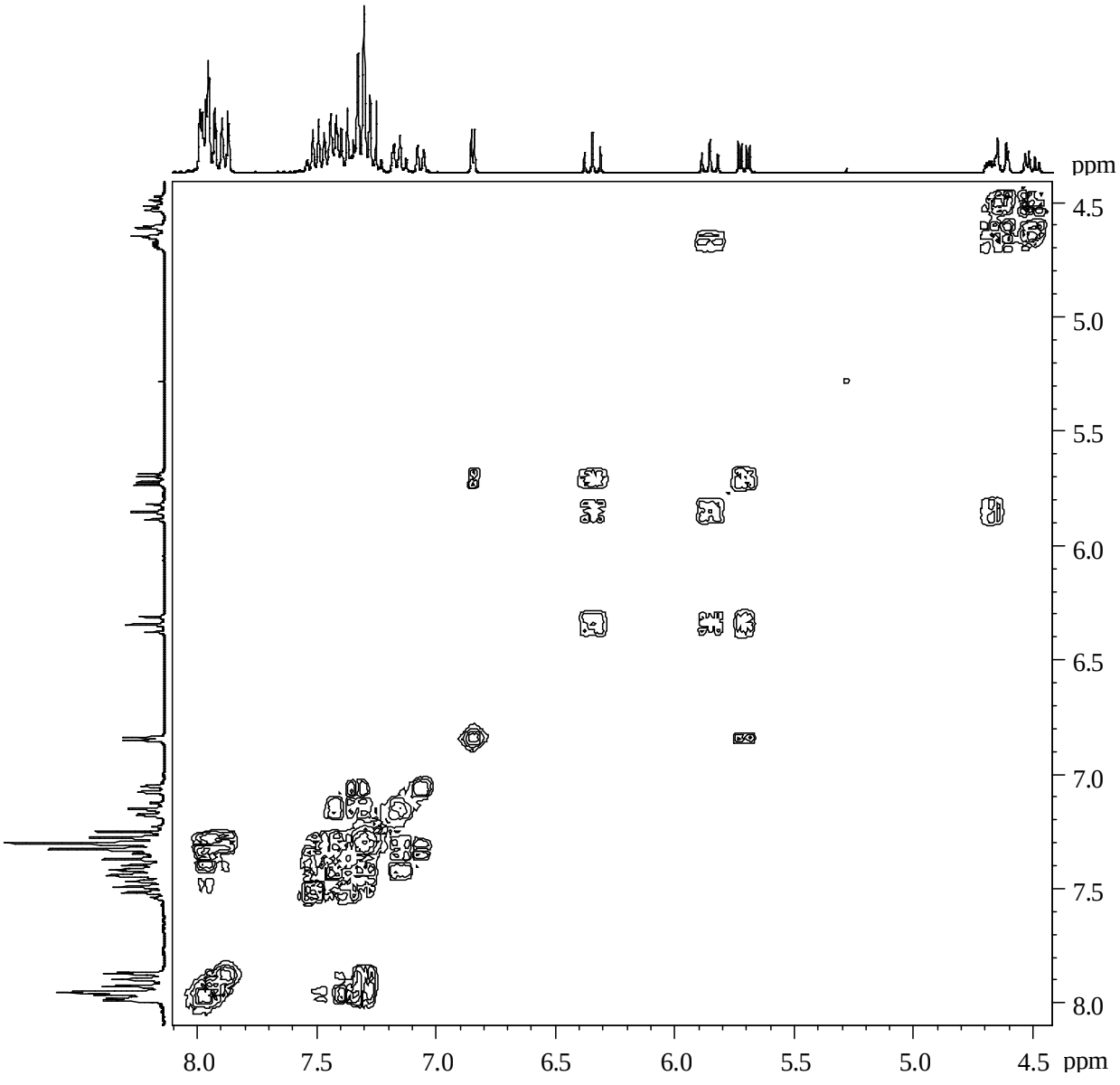
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)

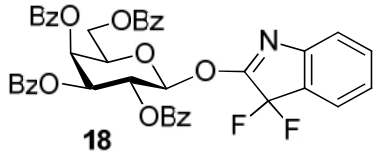


16

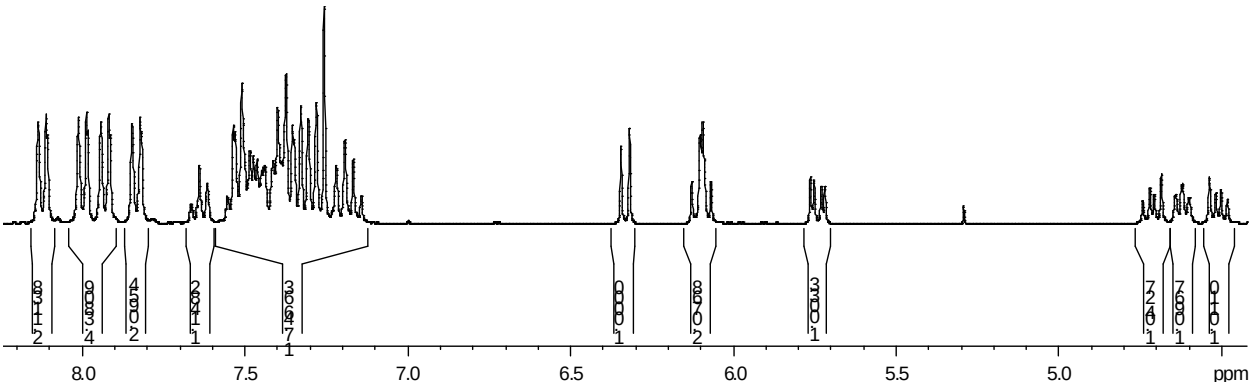


(2D NMR 300 MHz, $CDCl_3$)

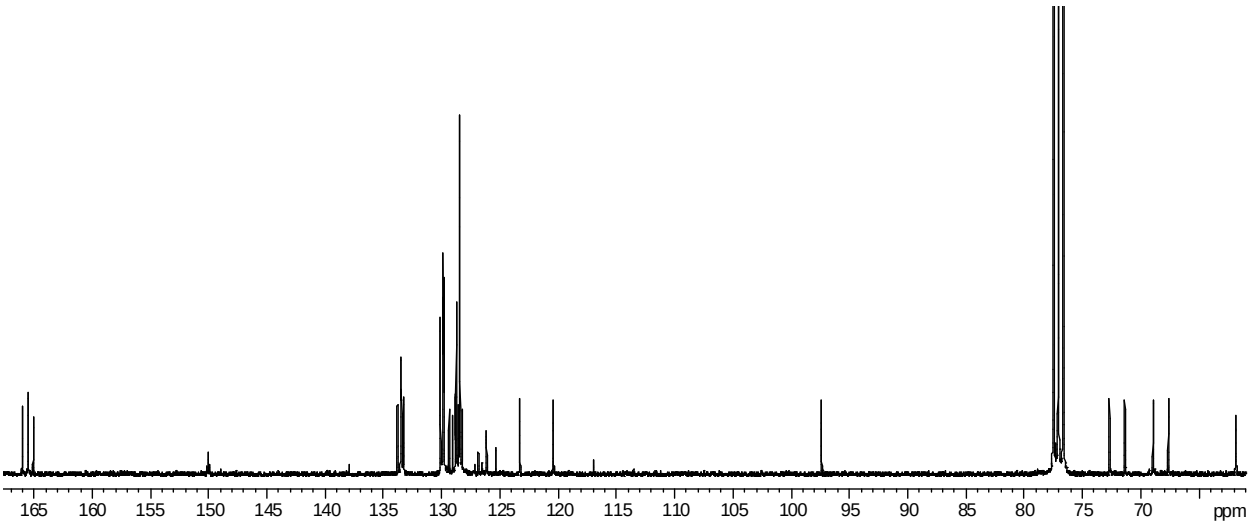
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (18)



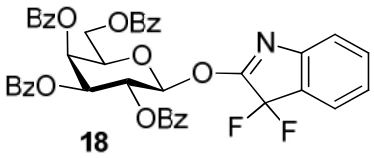
18



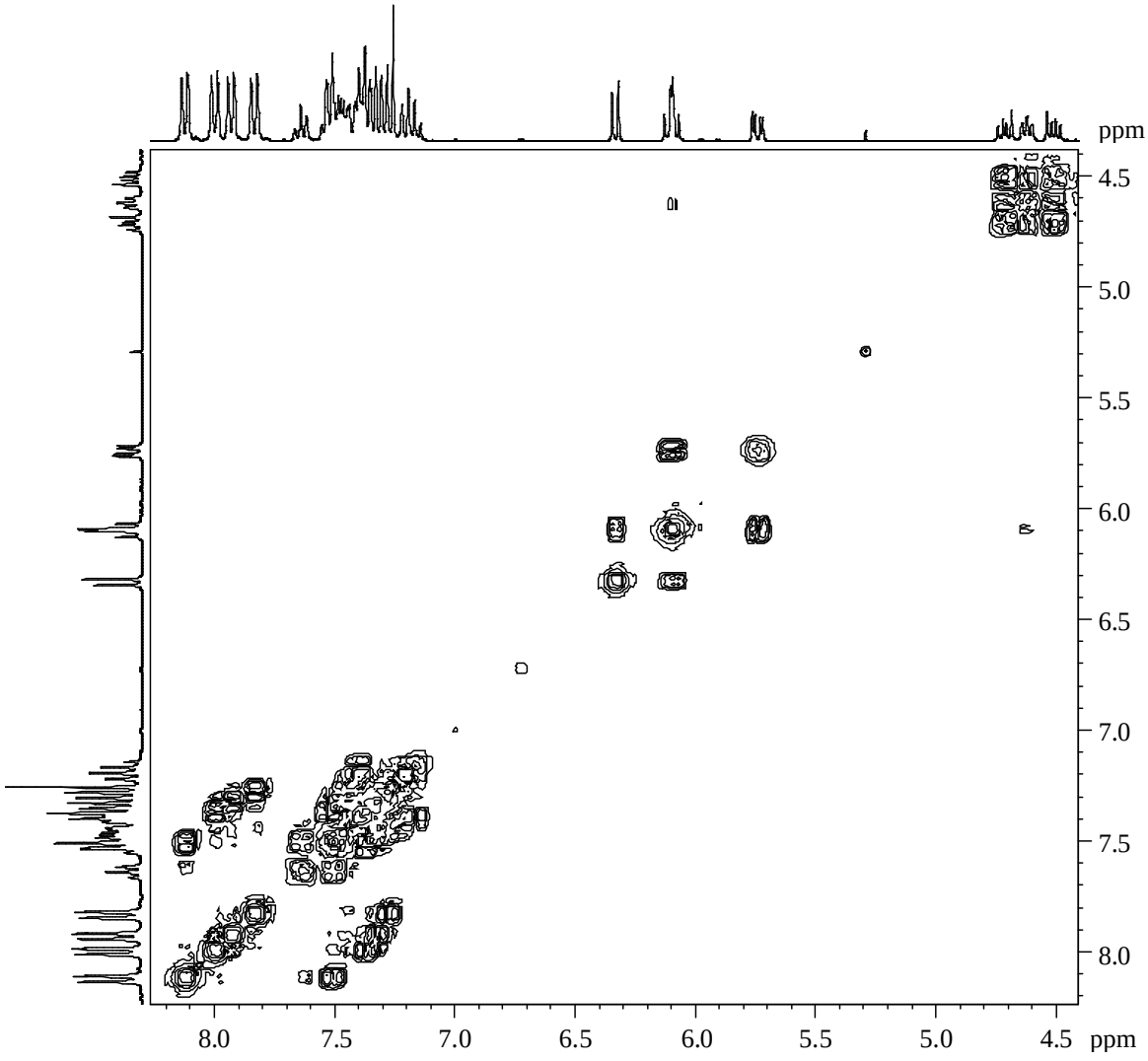
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)

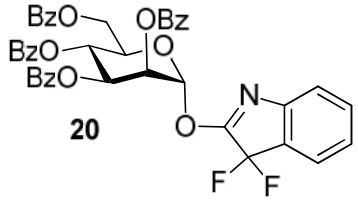


18

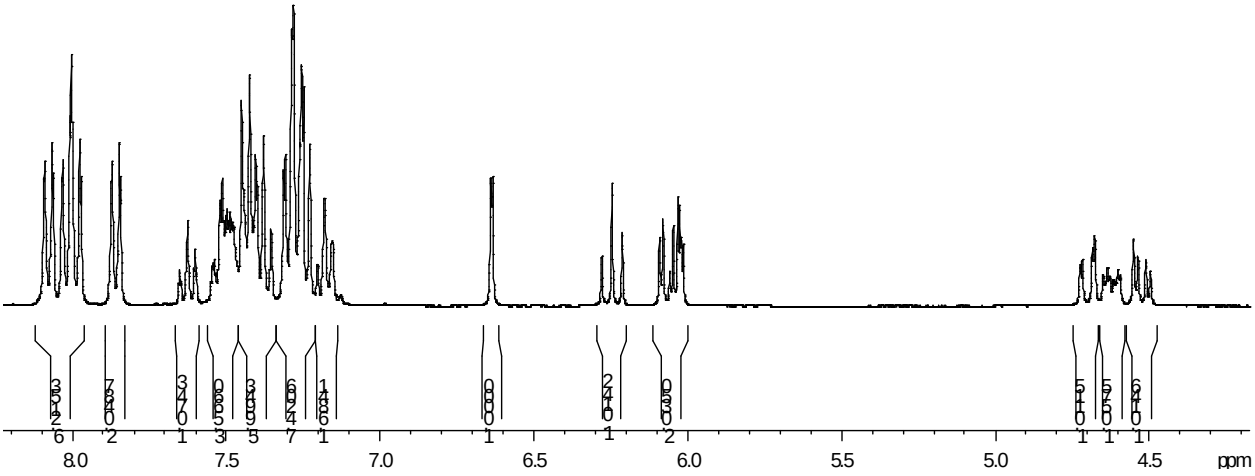


(2D NMR 300 MHz, $CDCl_3$)

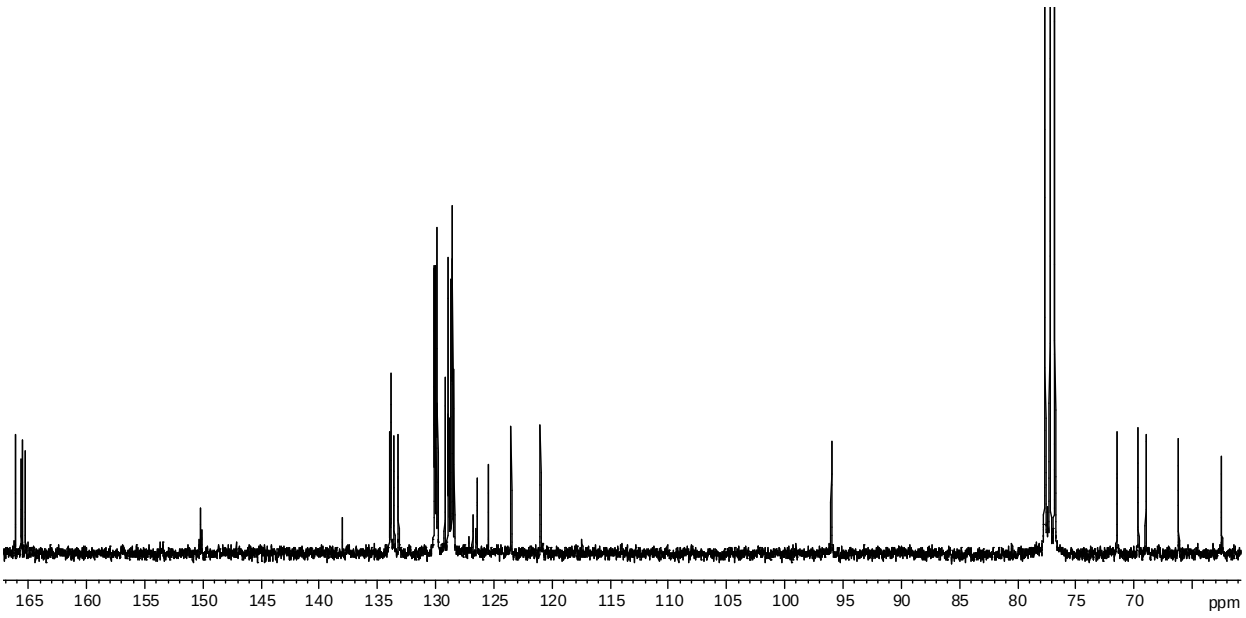
3,3-Difluoro-3*H*-indol-2-yl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (20)



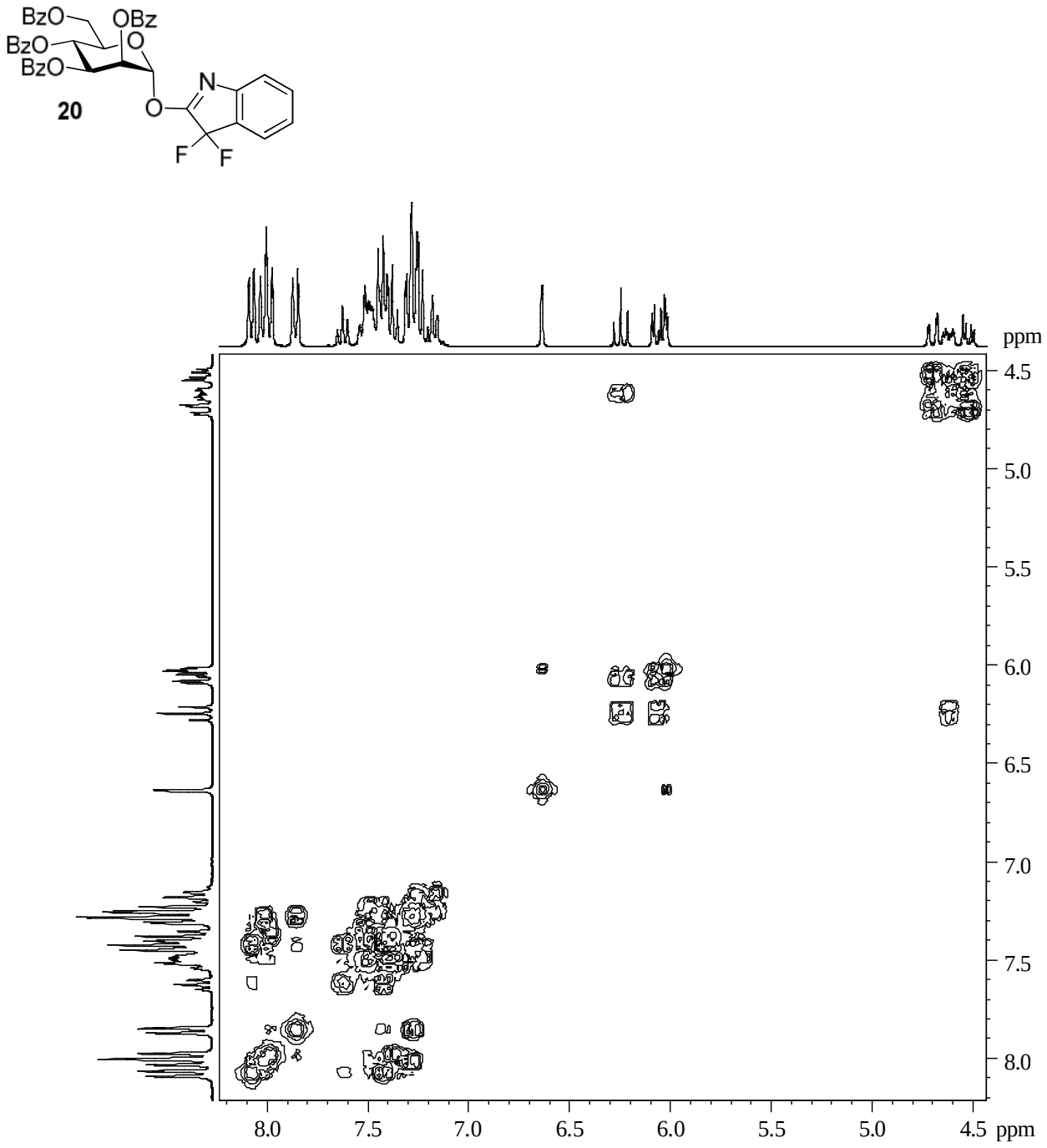
20



(^{1}H NMR 300 MHz, $CDCl_3$)

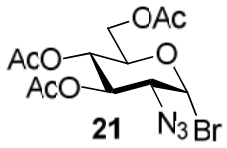


(^{13}C NMR 75 MHz, $CDCl_3$)

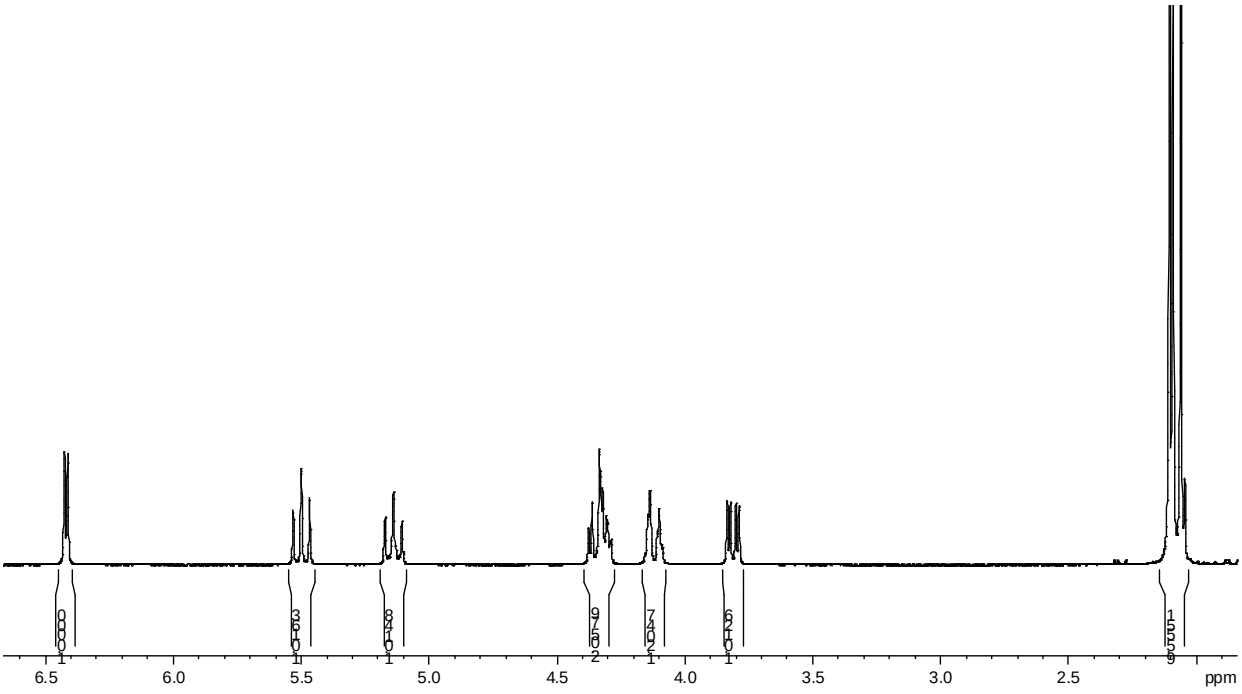


(2D NMR 300 MHz, $CDCl_3$)

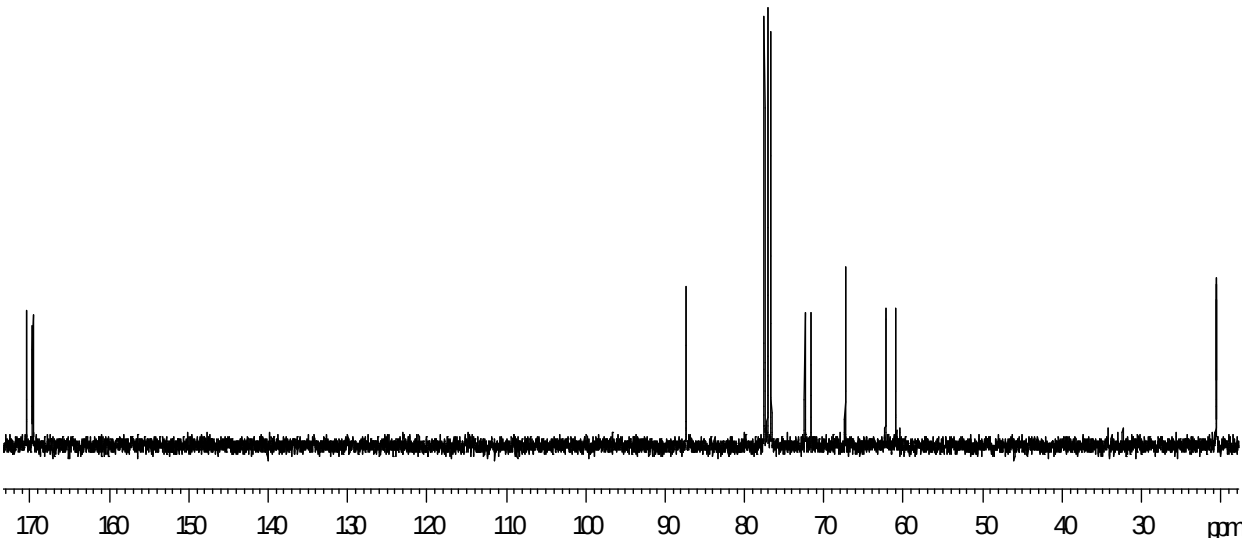
3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl bromide (21)



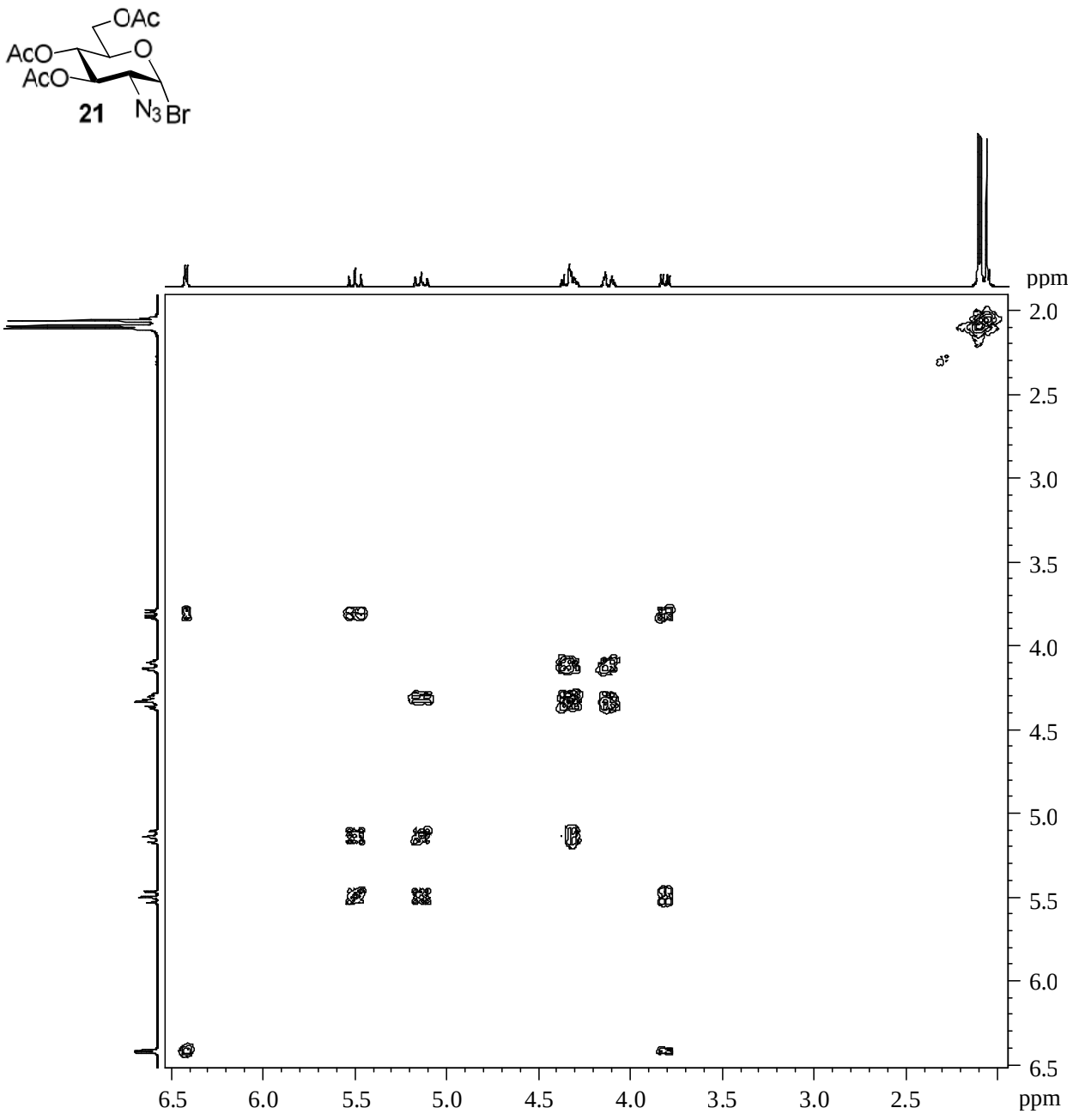
21



(^{1}H NMR 300 MHz, $CDCl_3$)

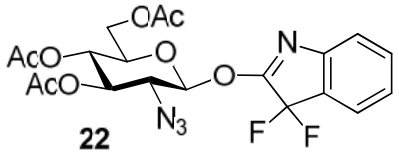


(^{13}C NMR 75 MHz, $CDCl_3$)



(2D NMR 300 MHz, $CDCl_3$)

3,3-Difluoro-3*H*-indol-2-yl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (22)



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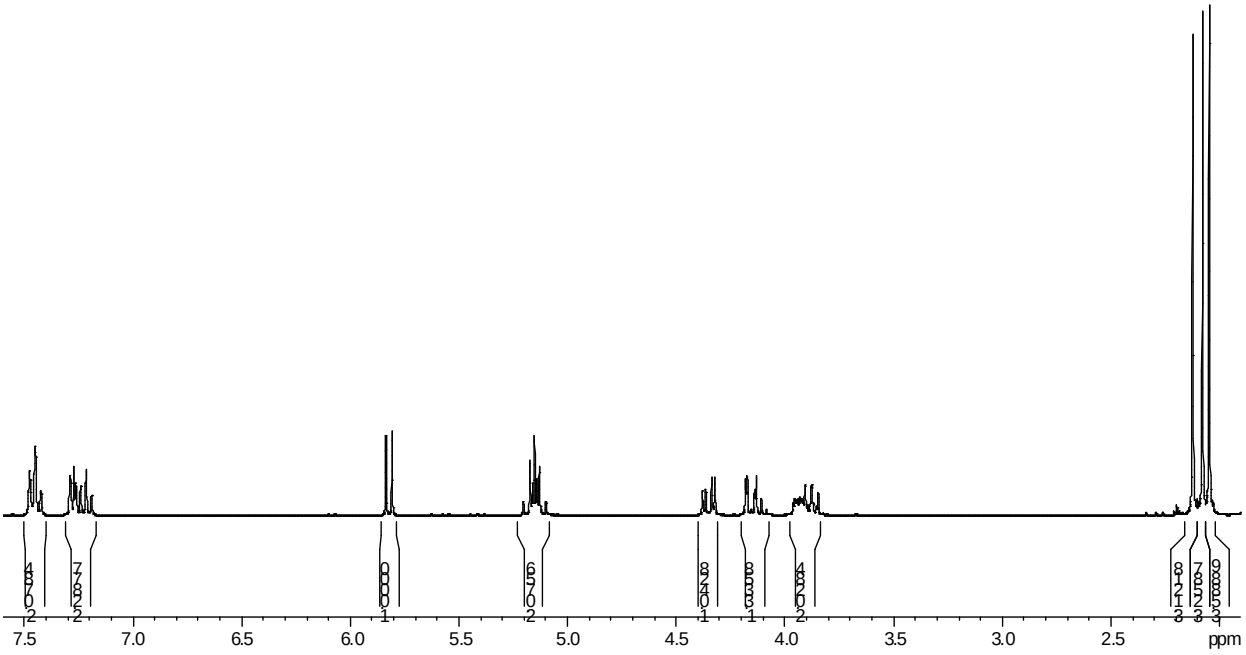
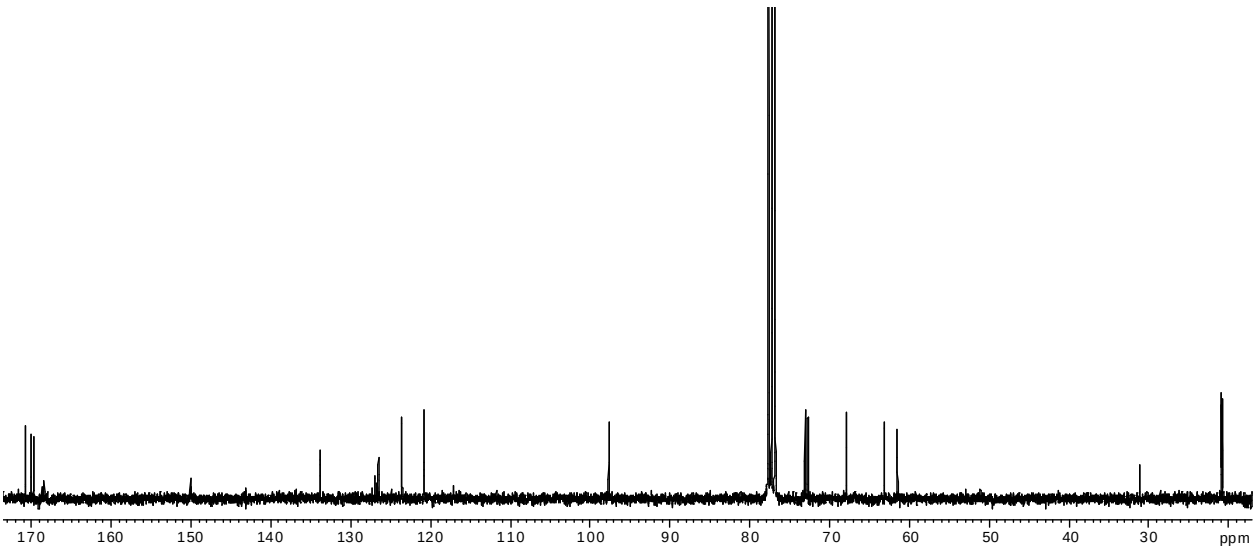
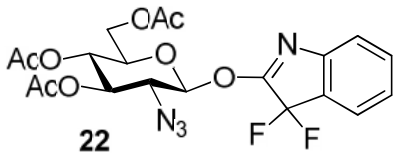


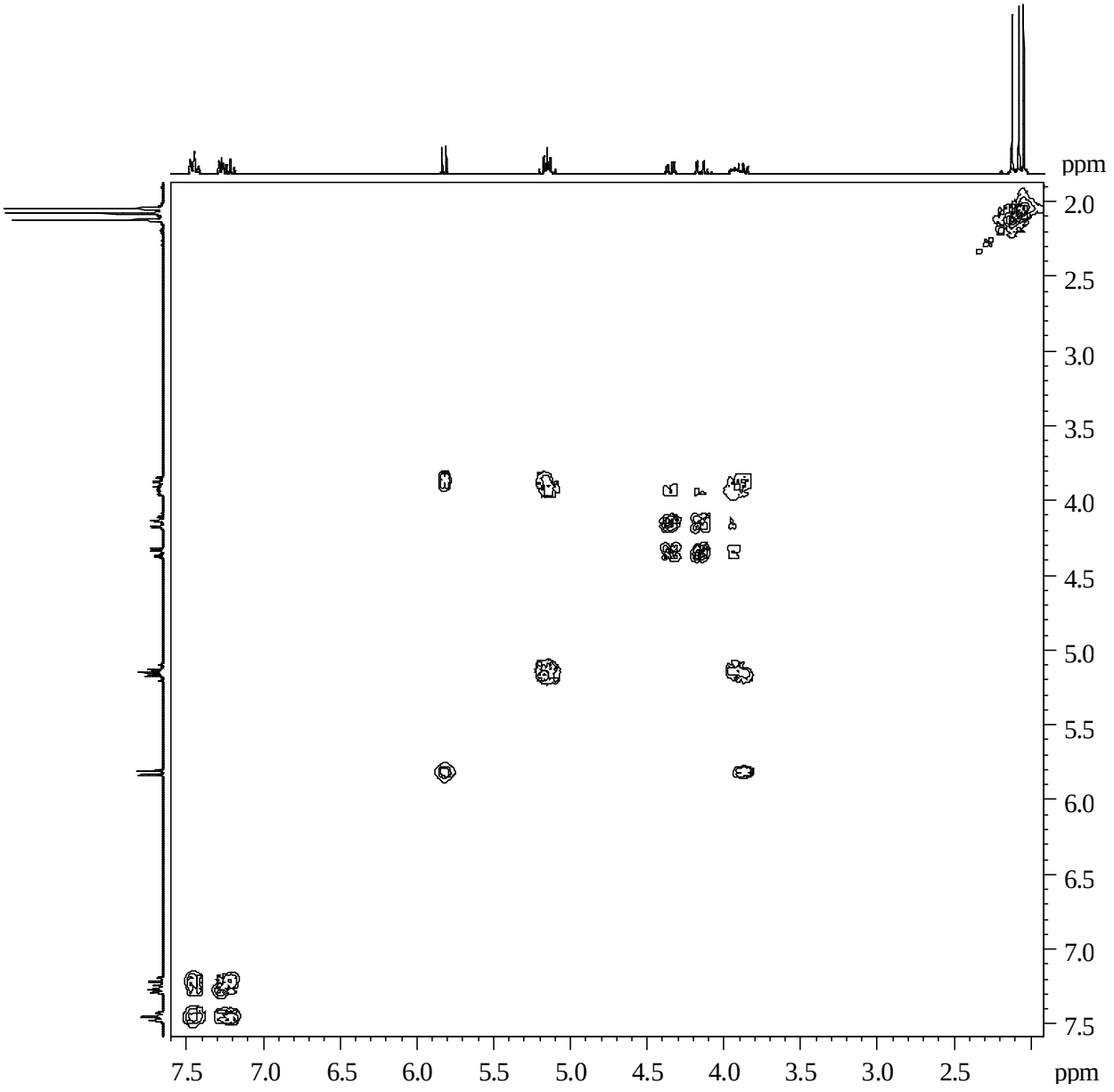
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)

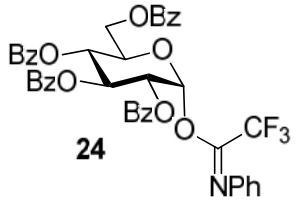


22

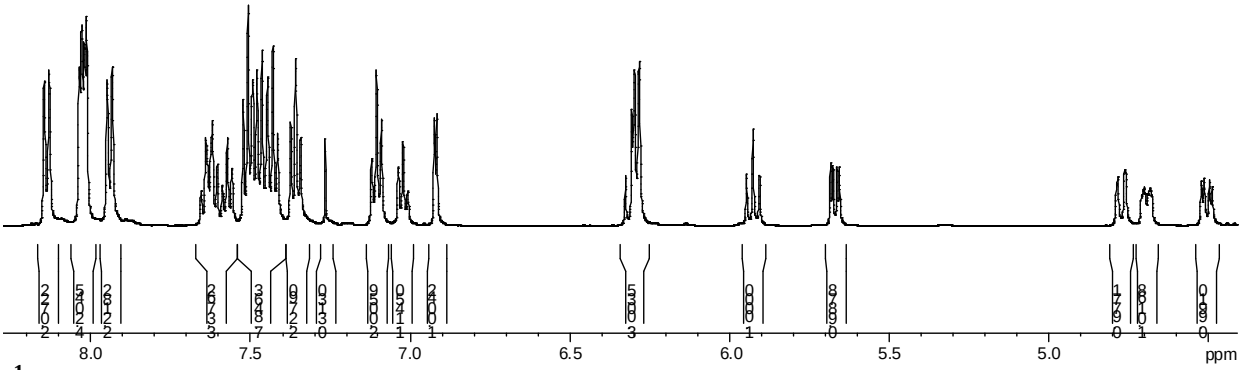


(2D NMR 300 MHz, $CDCl_3$)

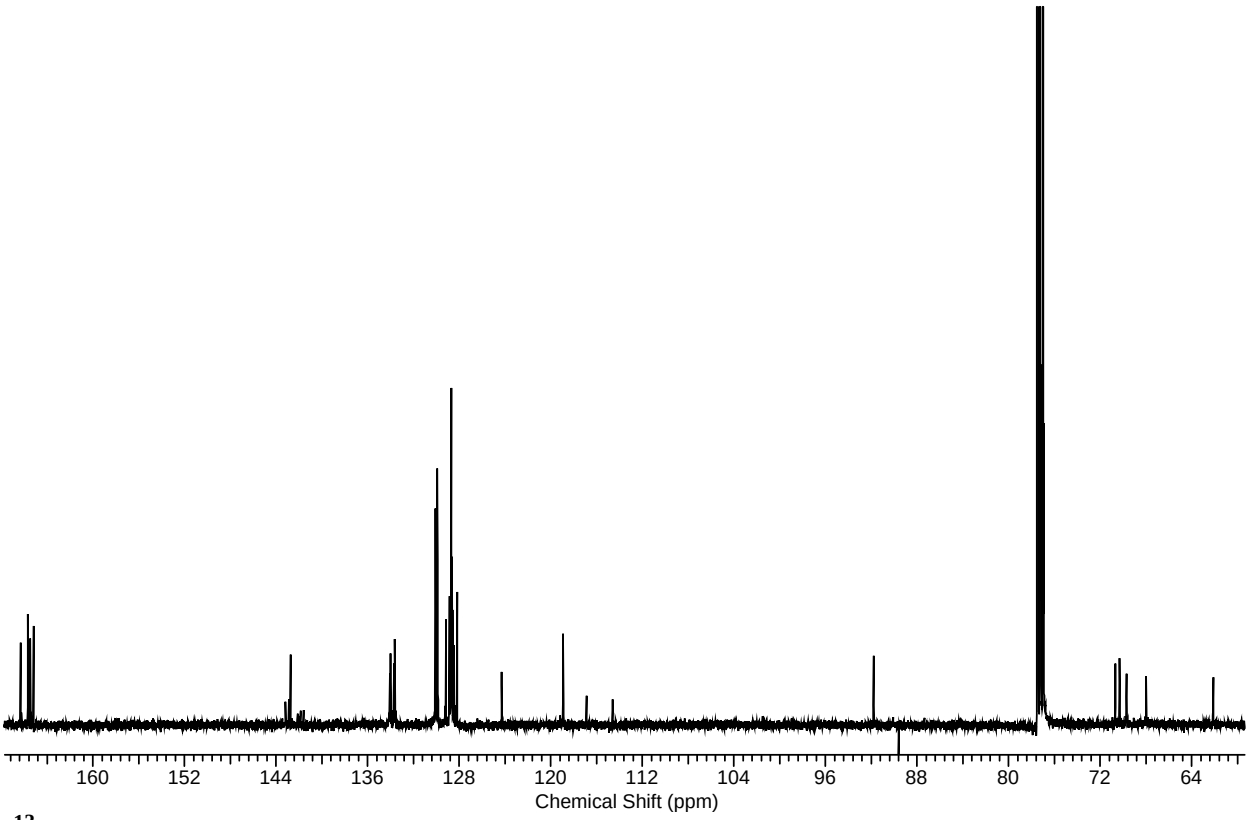
2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl N-phenyltrifluoroacetimidate (24)



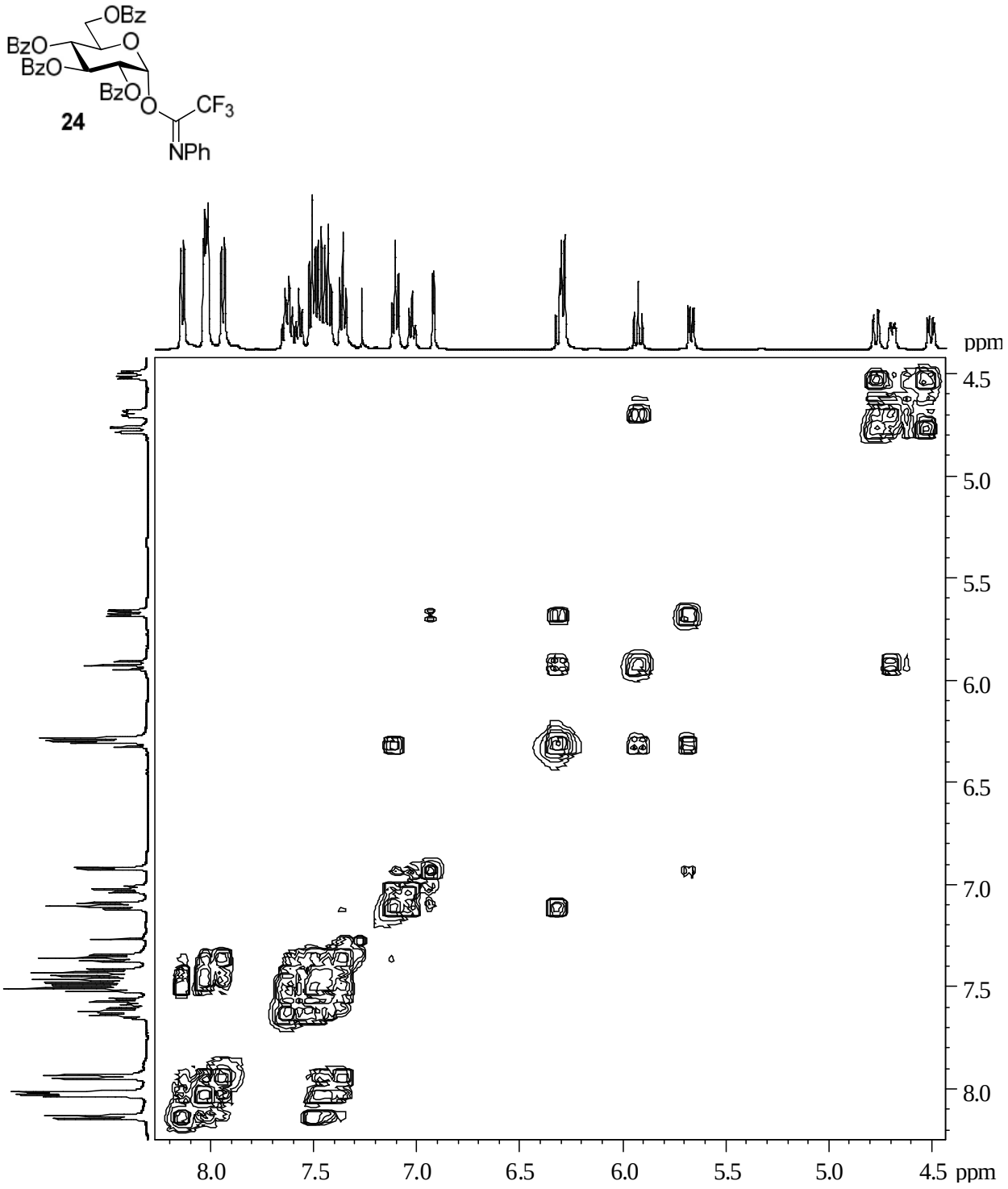
24



(^{1}H NMR 500 MHz, $CDCl_3$)

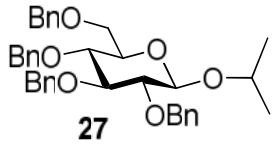


(^{13}C NMR 125 MHz, $CDCl_3$)

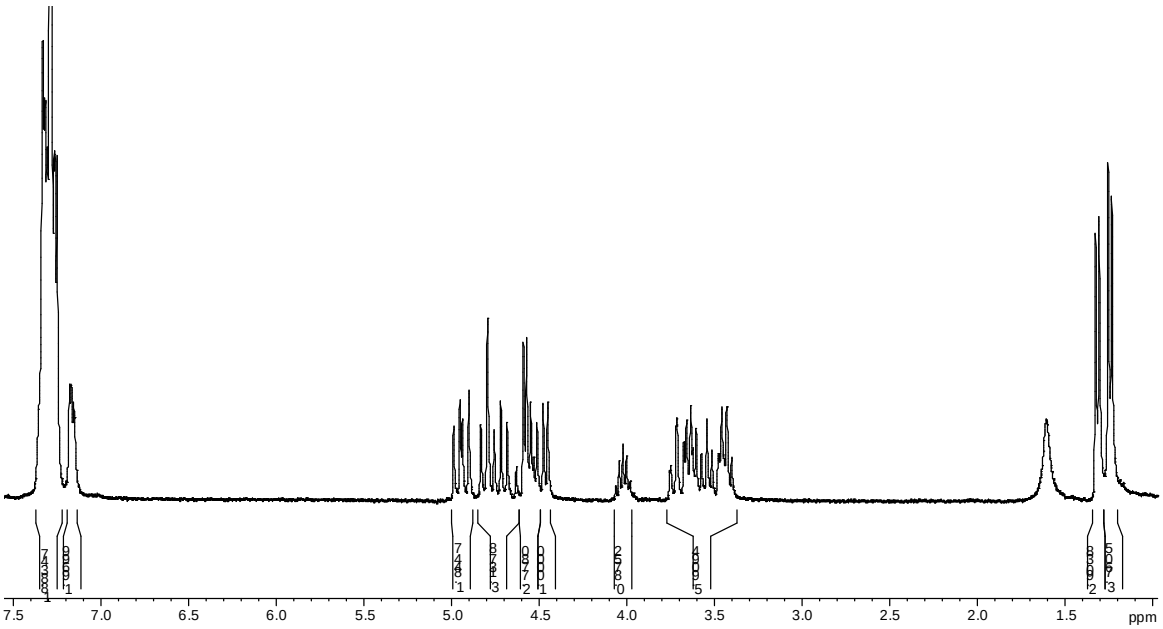


(2D NMR 500 MHz, $CDCl_3$)

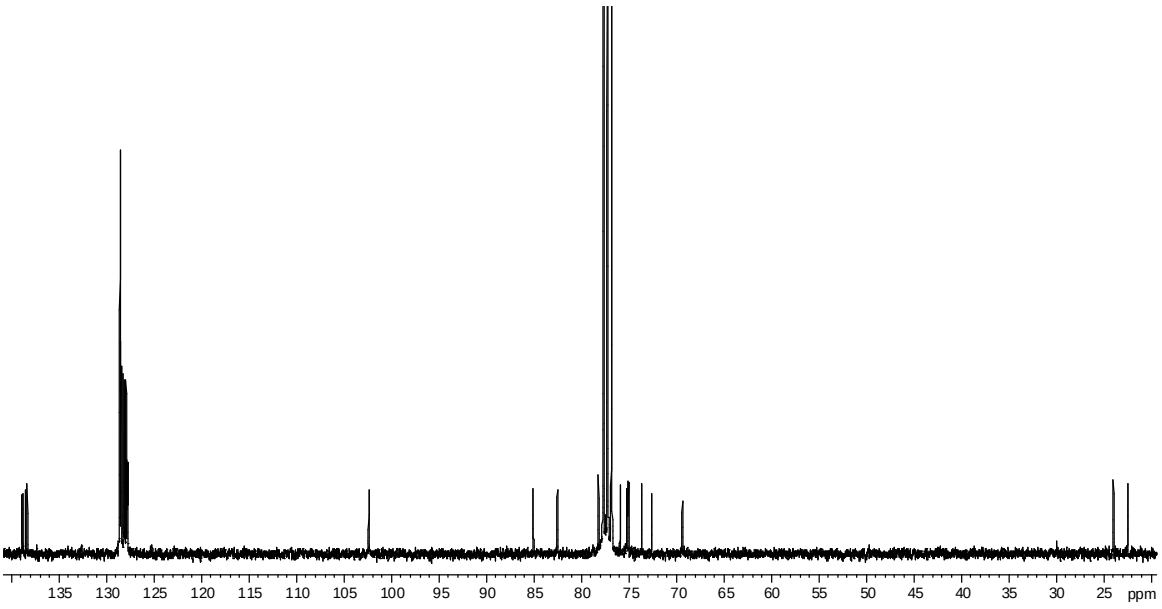
Isopropyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (27)



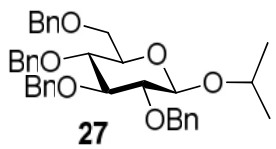
27



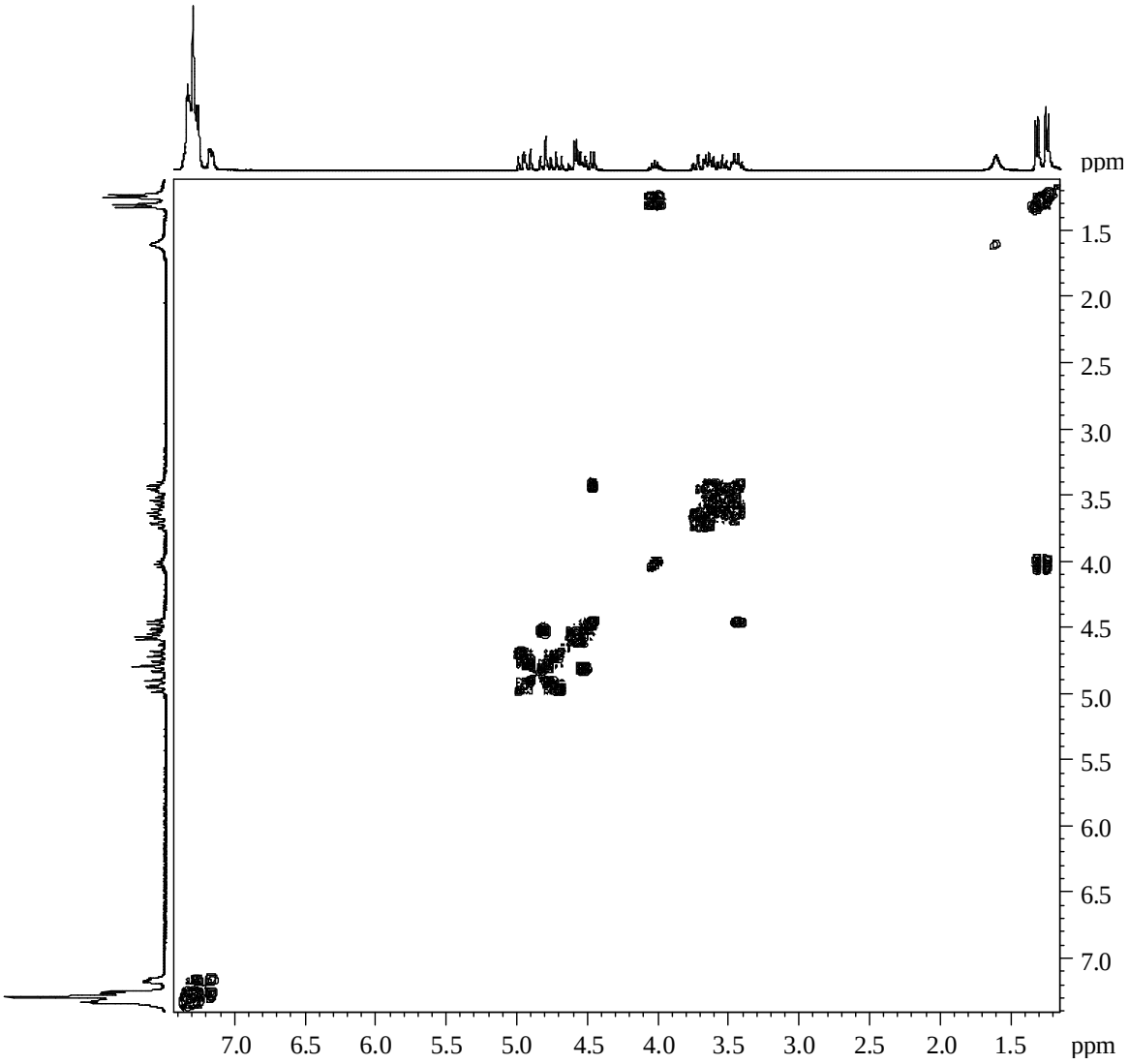
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)

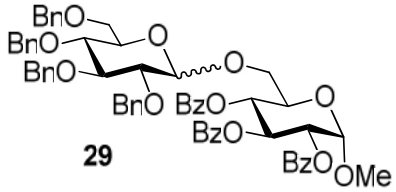


27

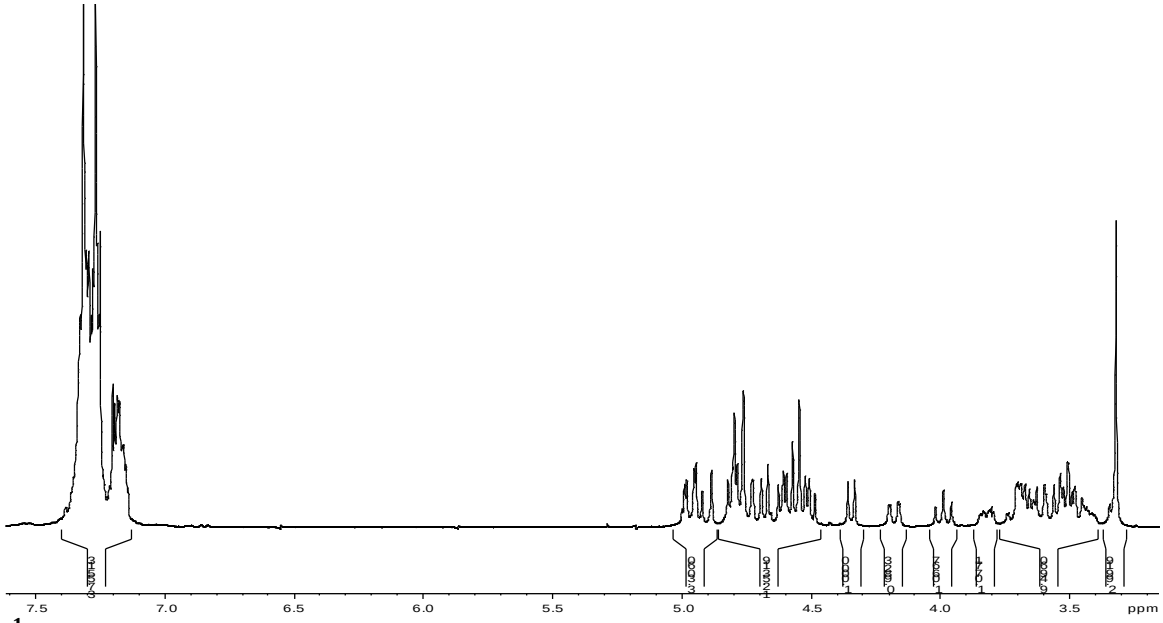


(2D NMR 300 MHz, $CDCl_3$)

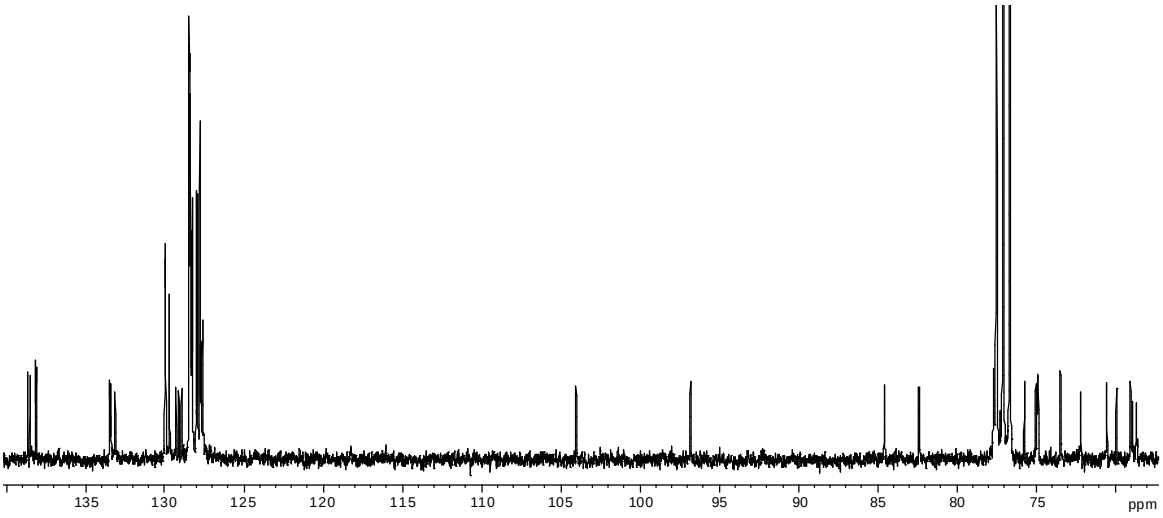
Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (29)



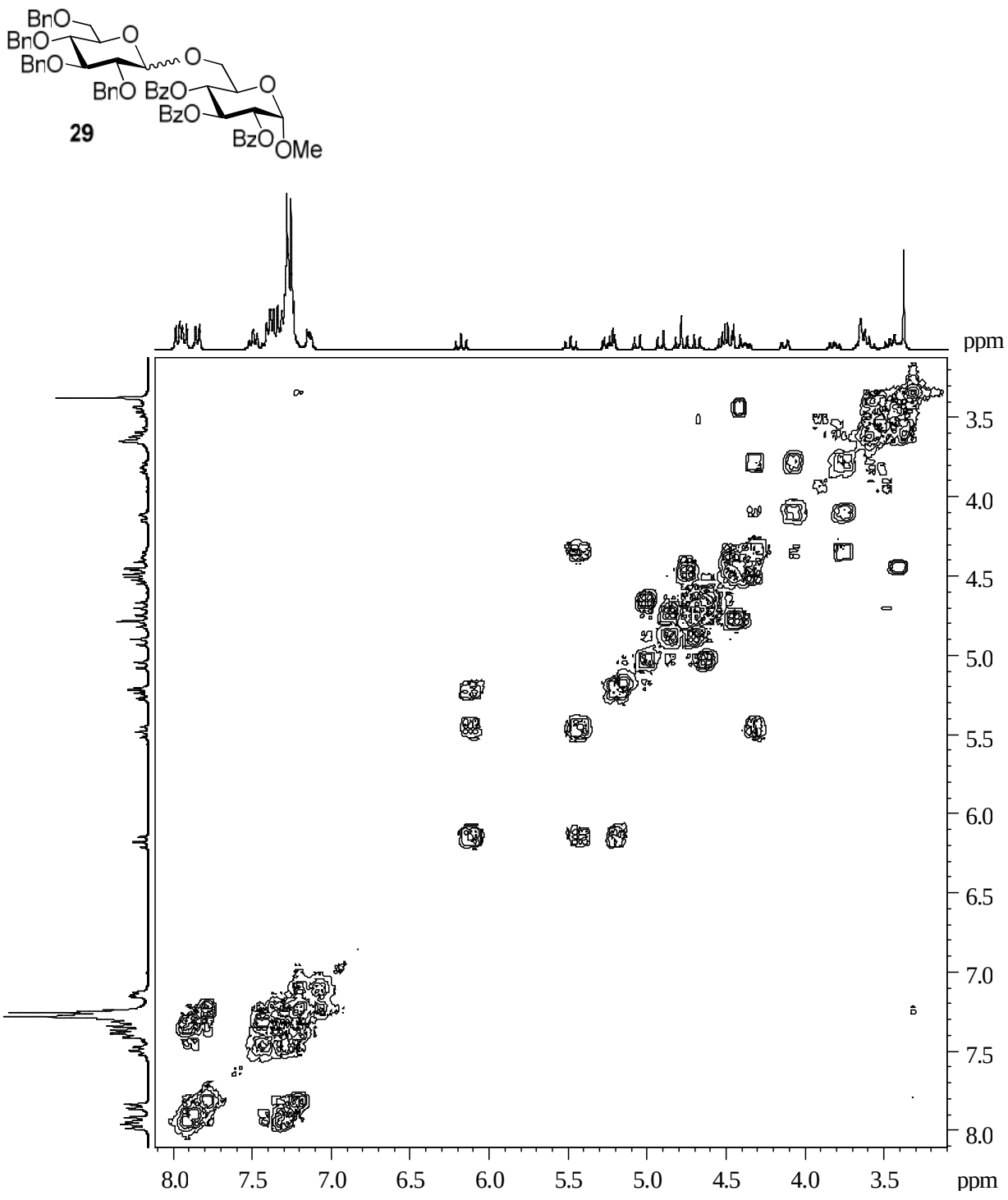
29



(^{1}H NMR 300 MHz, $CDCl_3$)

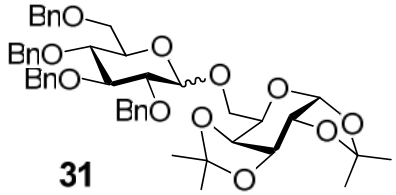


(^{13}C NMR 75 MHz, $CDCl_3$)

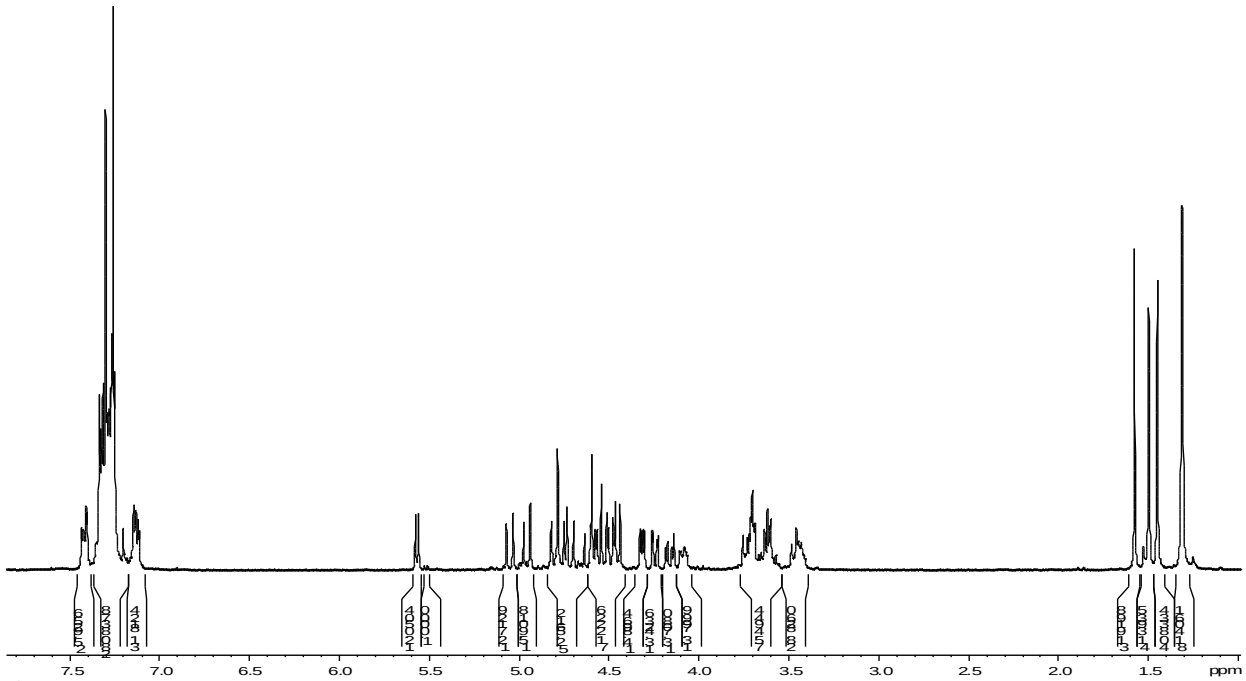


(2D NMR 300 MHz, $CDCl_3$)

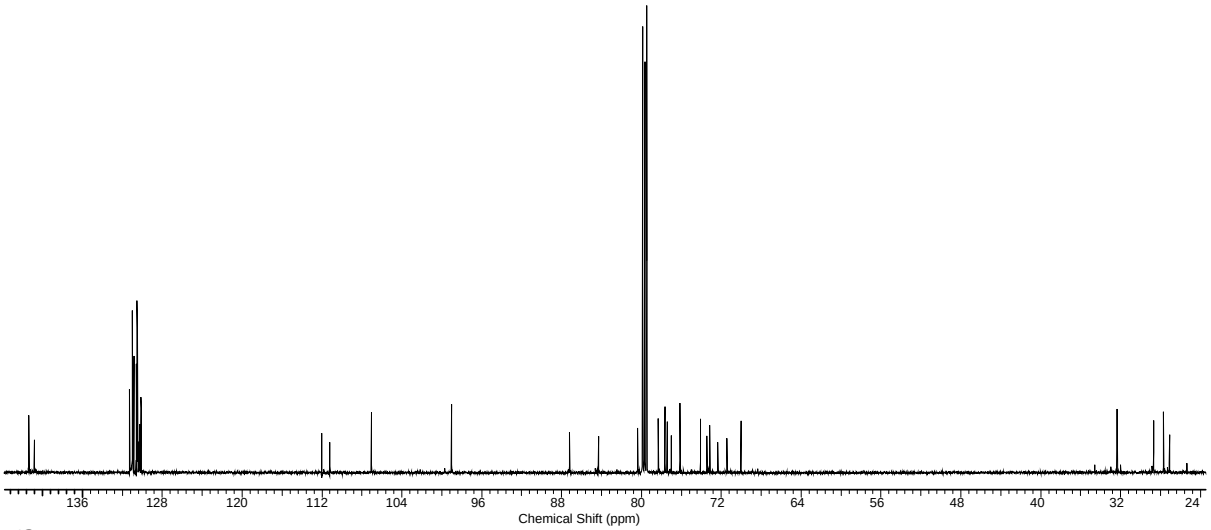
6-*O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (31)



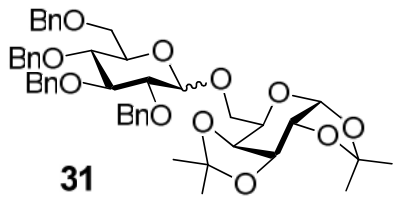
31



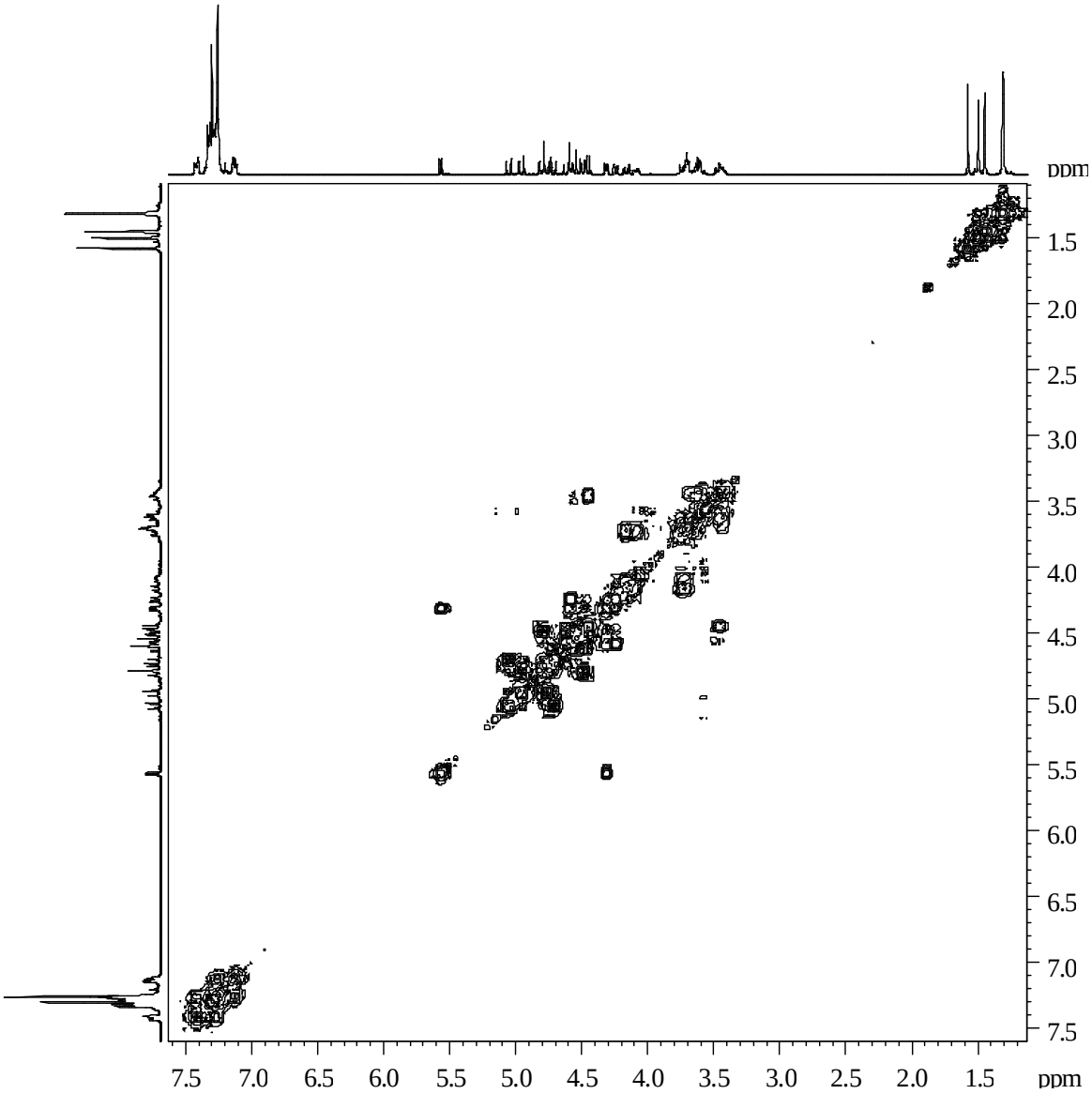
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 150 MHz, $CDCl_3$)

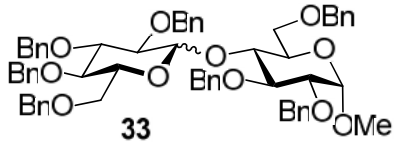


31

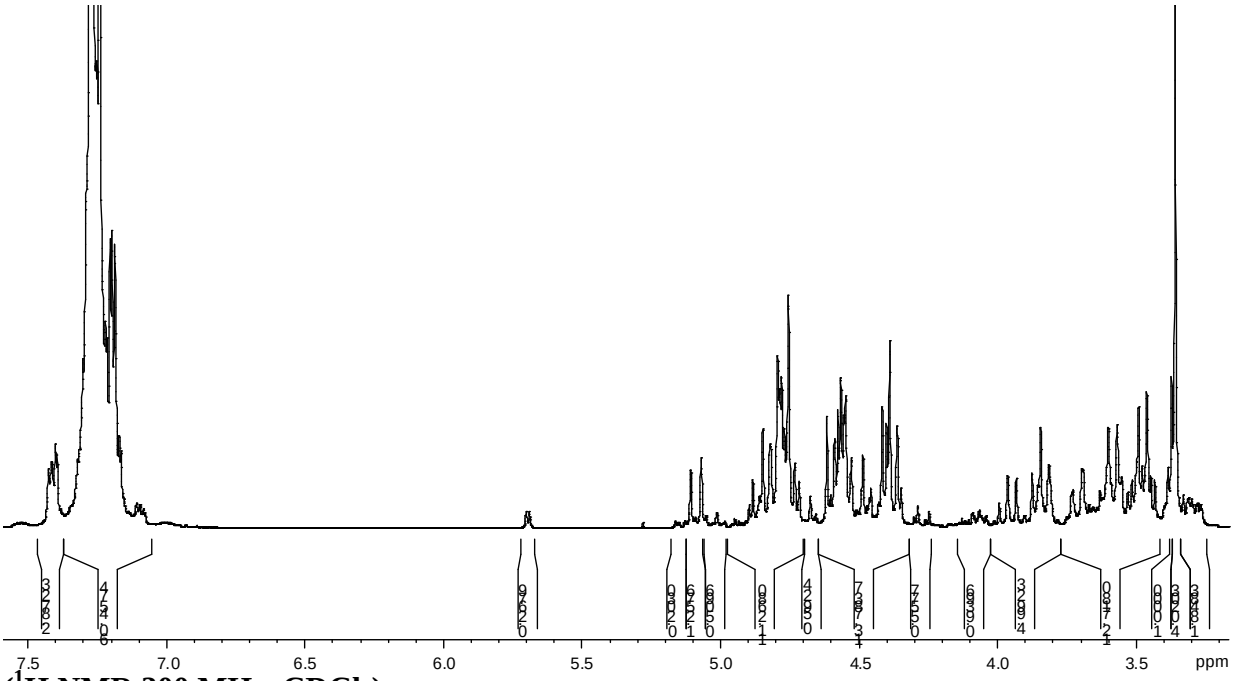


(2D NMR 300 MHz, $CDCl_3$)

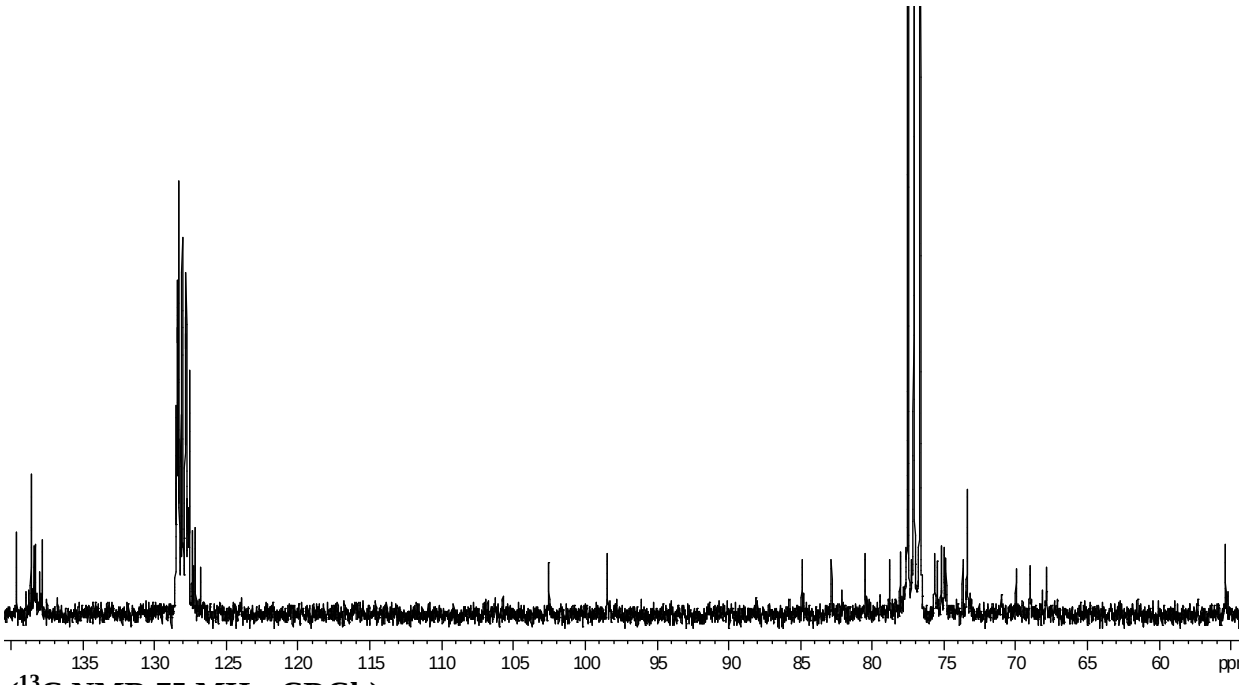
Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (33)



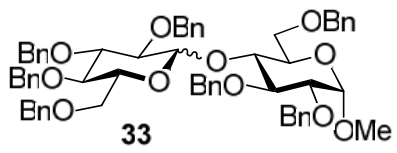
33



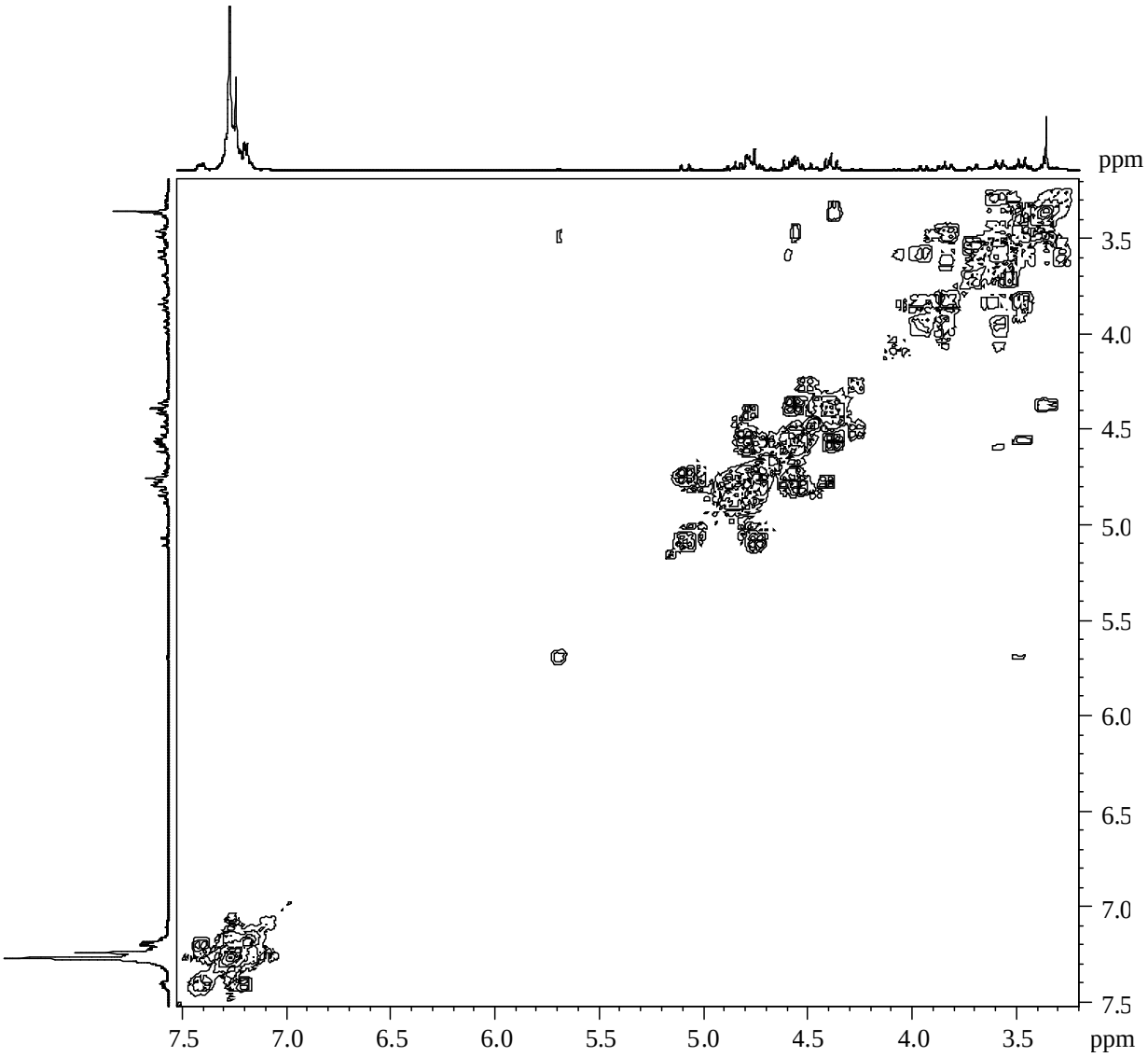
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)

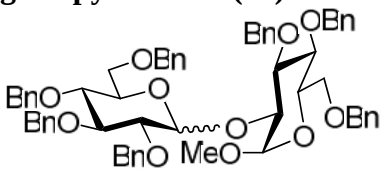


33



(2D NMR 300 MHz, $CDCl_3$)

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (35)



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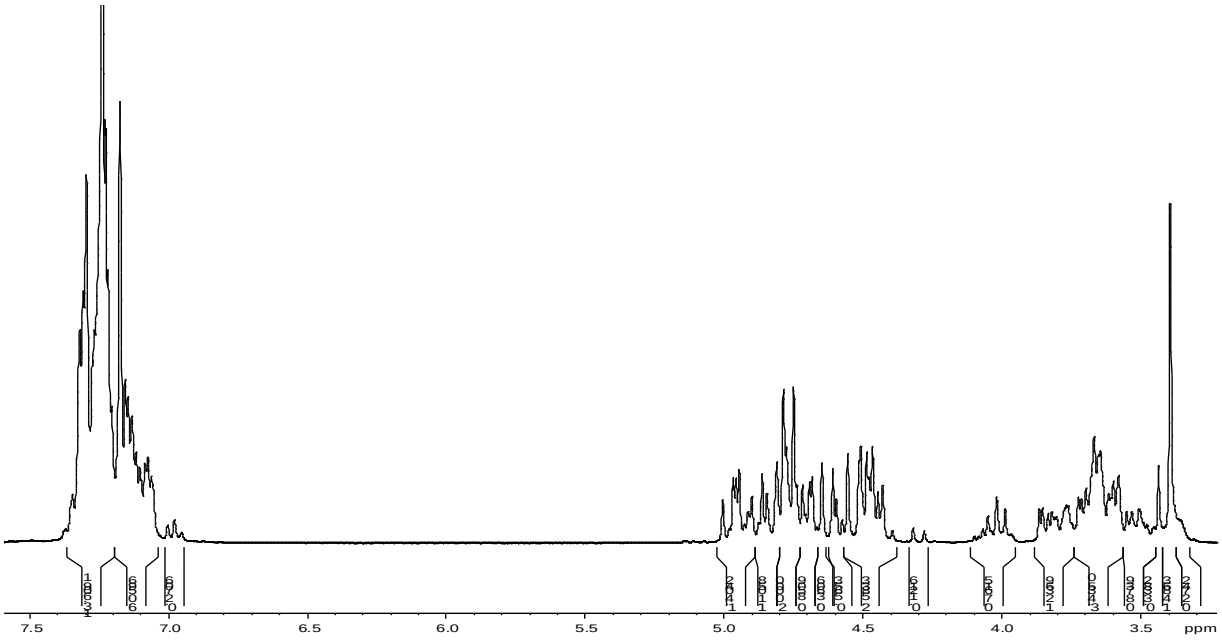
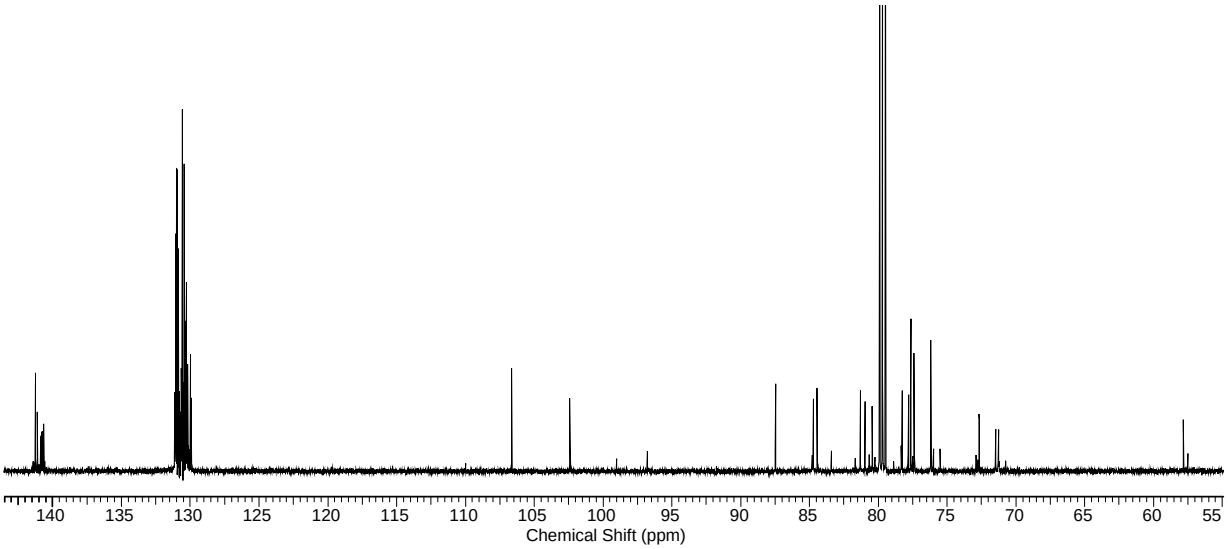
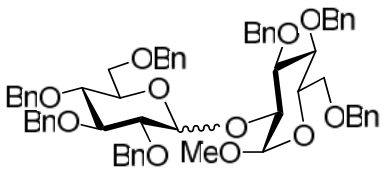


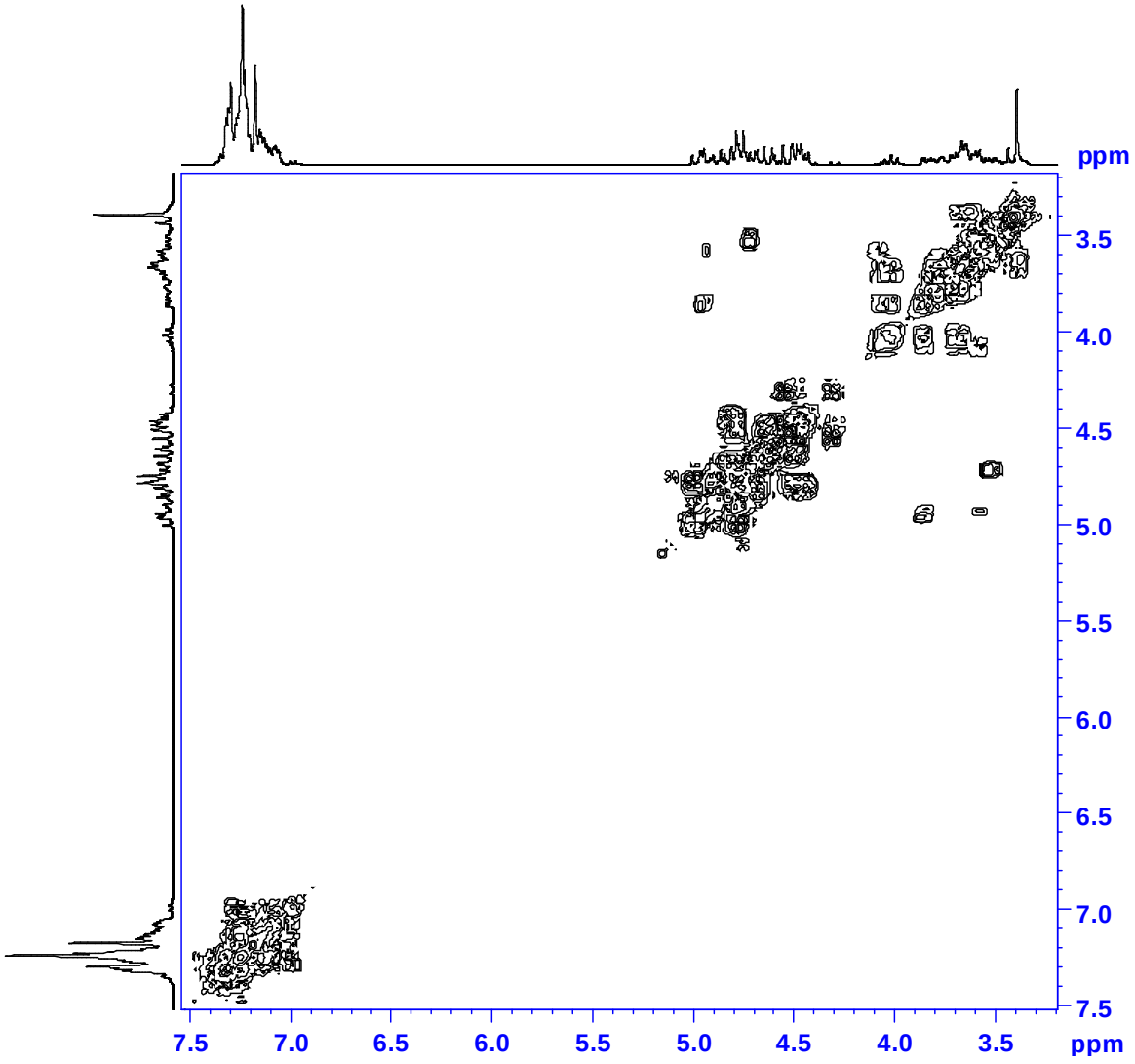
(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 150 MHz, $CDCl_3$)

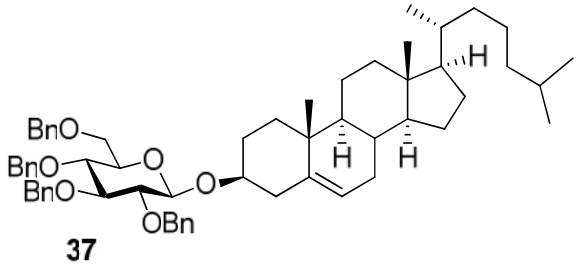


35

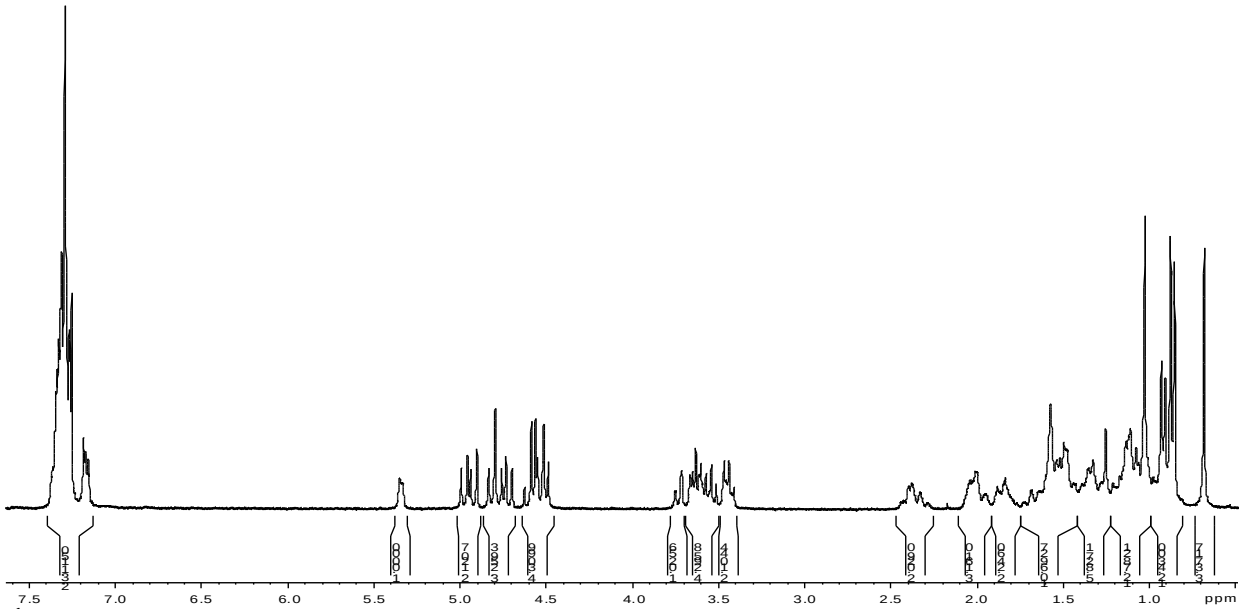


(2D NMR 300 MHz, $CDCl_3$)

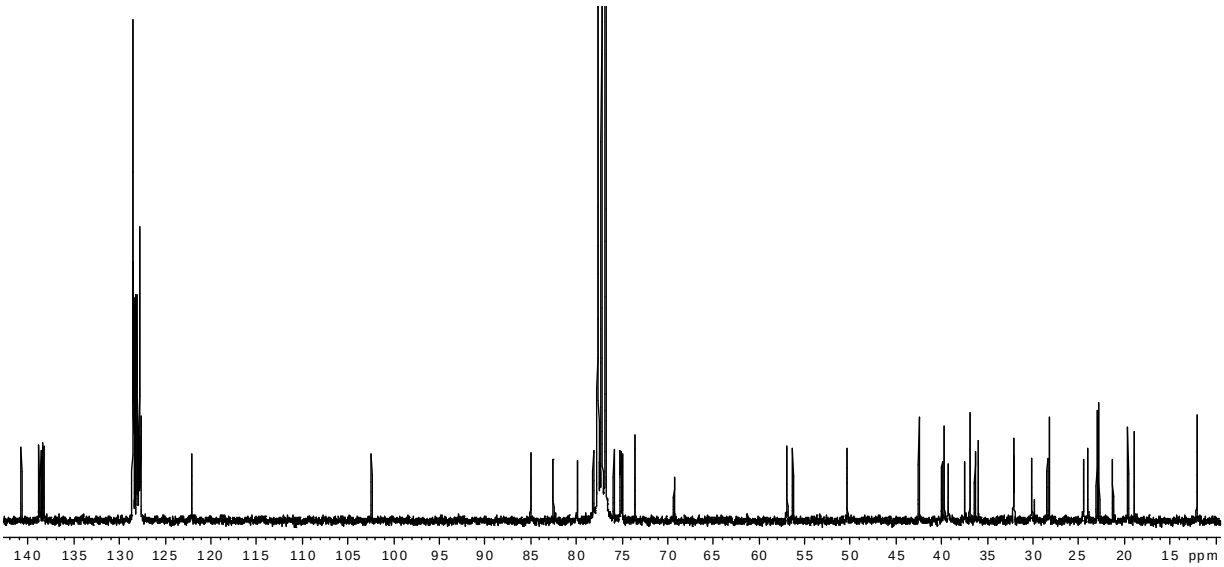
(3*β*)-Cholest-5-en-3-yl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (37)



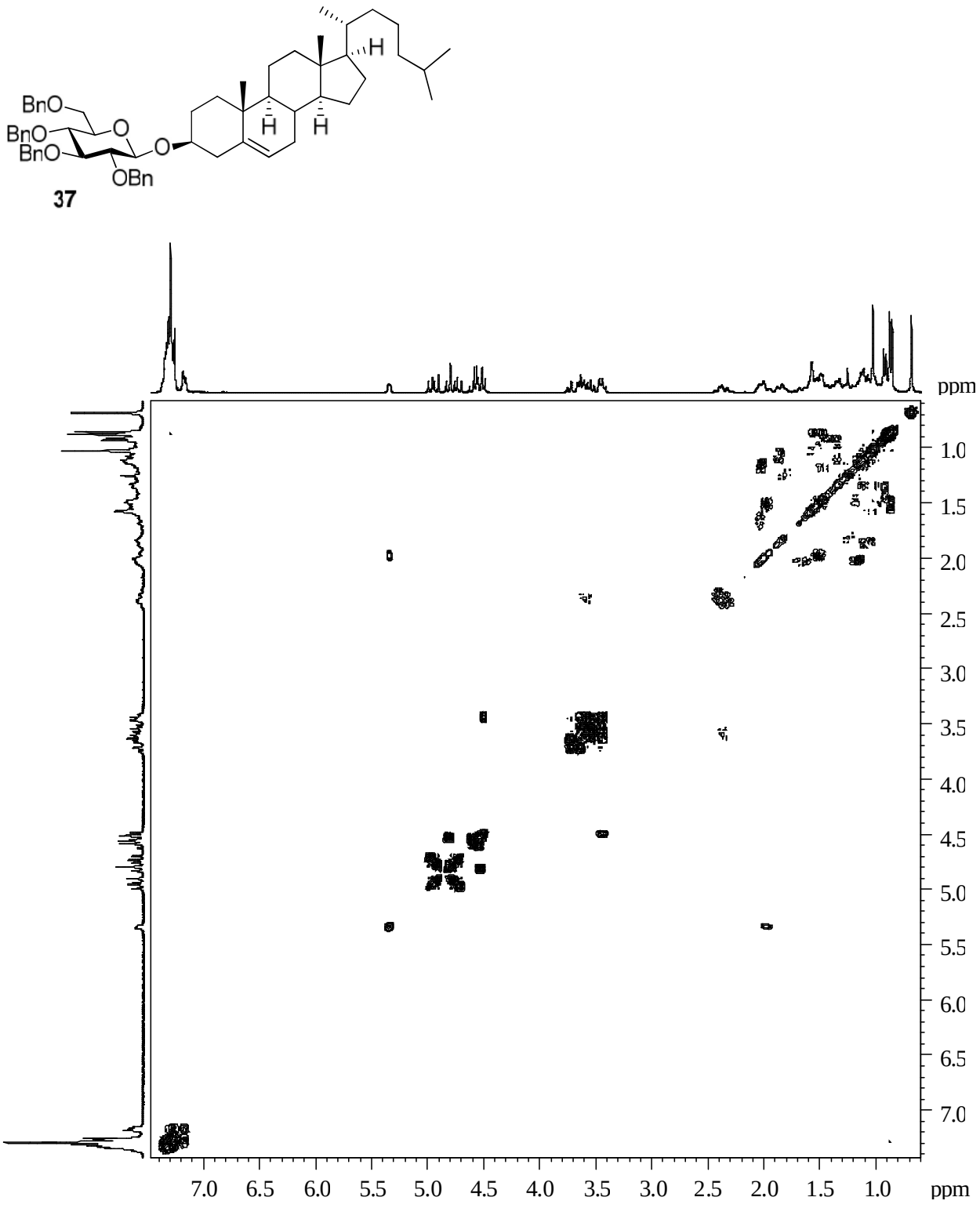
37



(^{1}H NMR 300 MHz, $CDCl_3$)



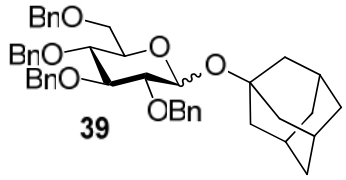
(^{13}C NMR 75 MHz, $CDCl_3$)



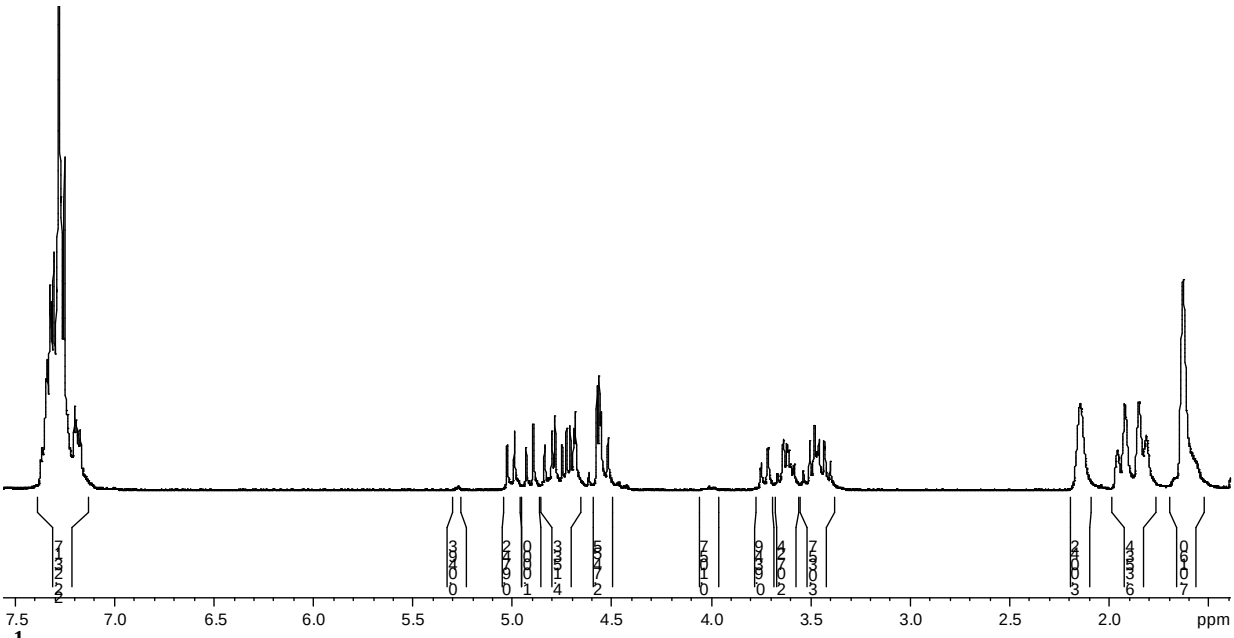
37

(2D NMR 300 MHz, $CDCl_3$)

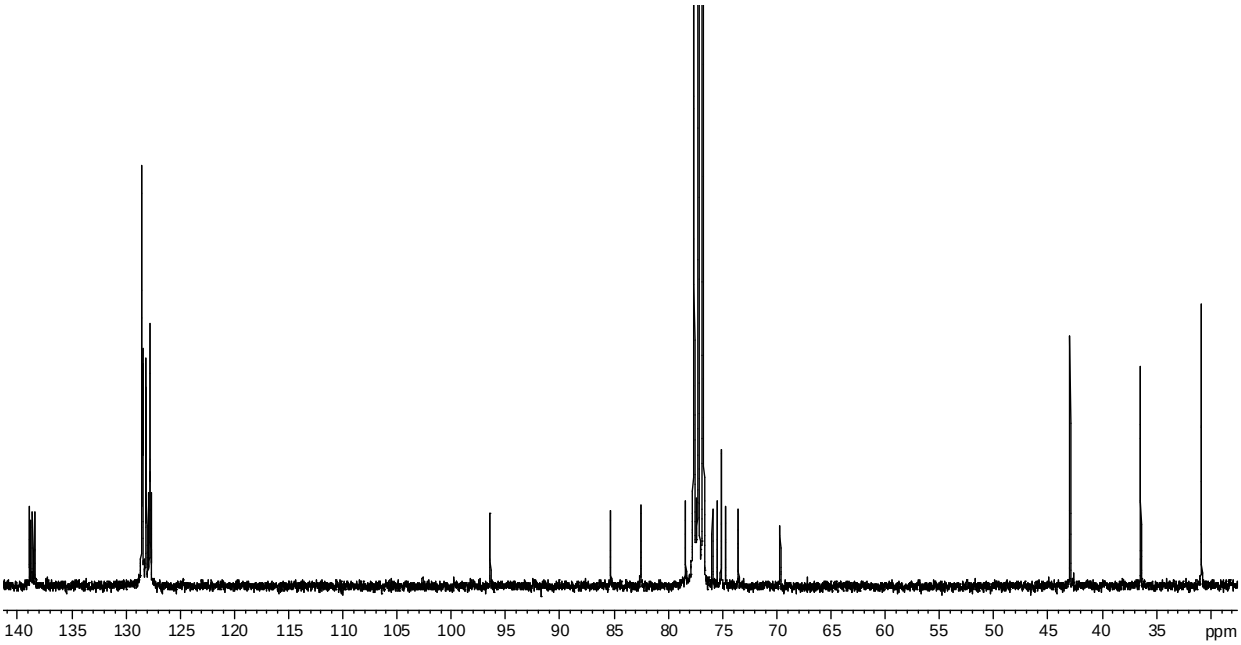
1-Adamantyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (39)



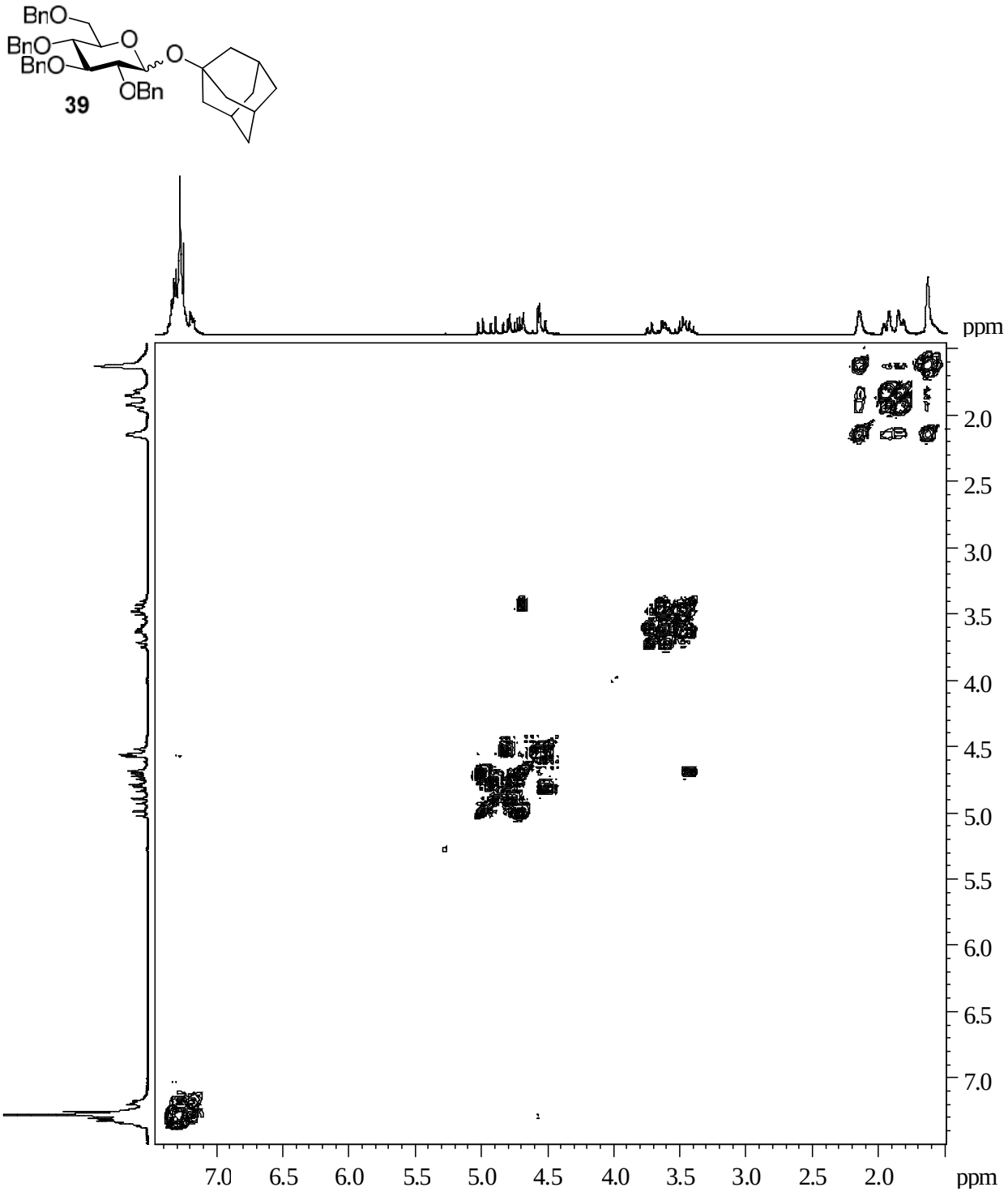
39



(^{1}H NMR 300 MHz, $CDCl_3$)

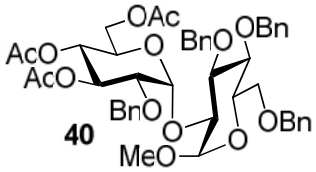


(^{13}C NMR 75 MHz, $CDCl_3$)

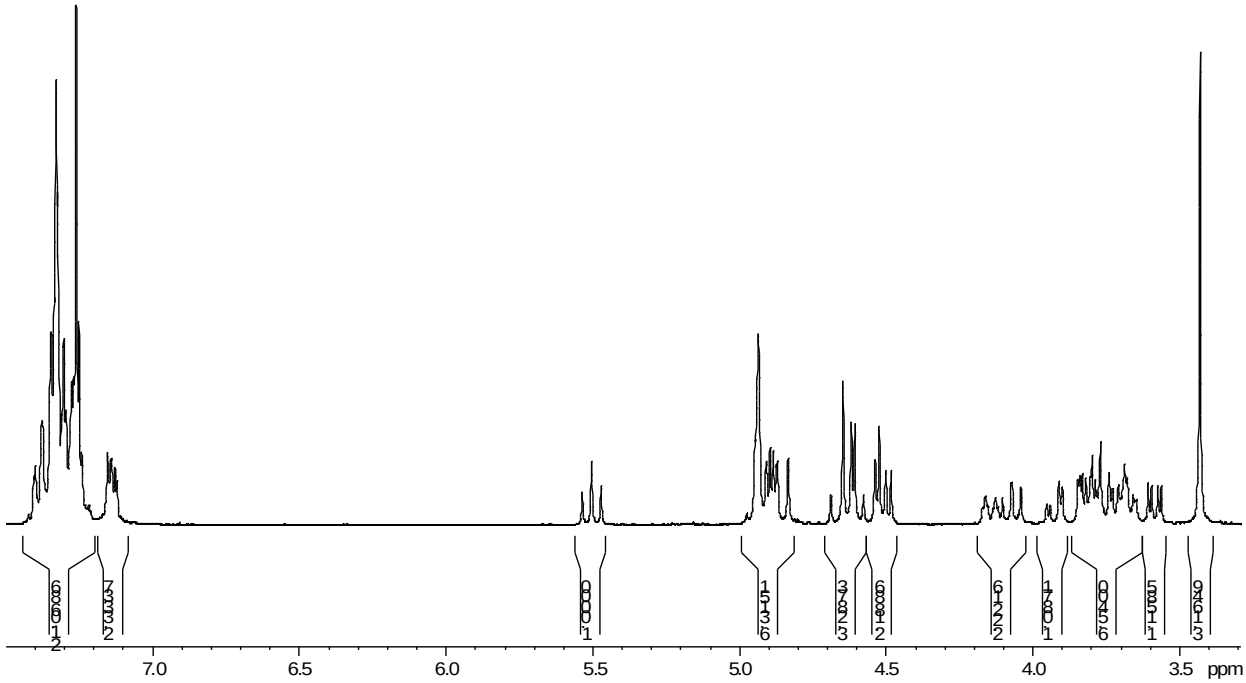


(2D NMR 300 MHz, $CDCl_3$)

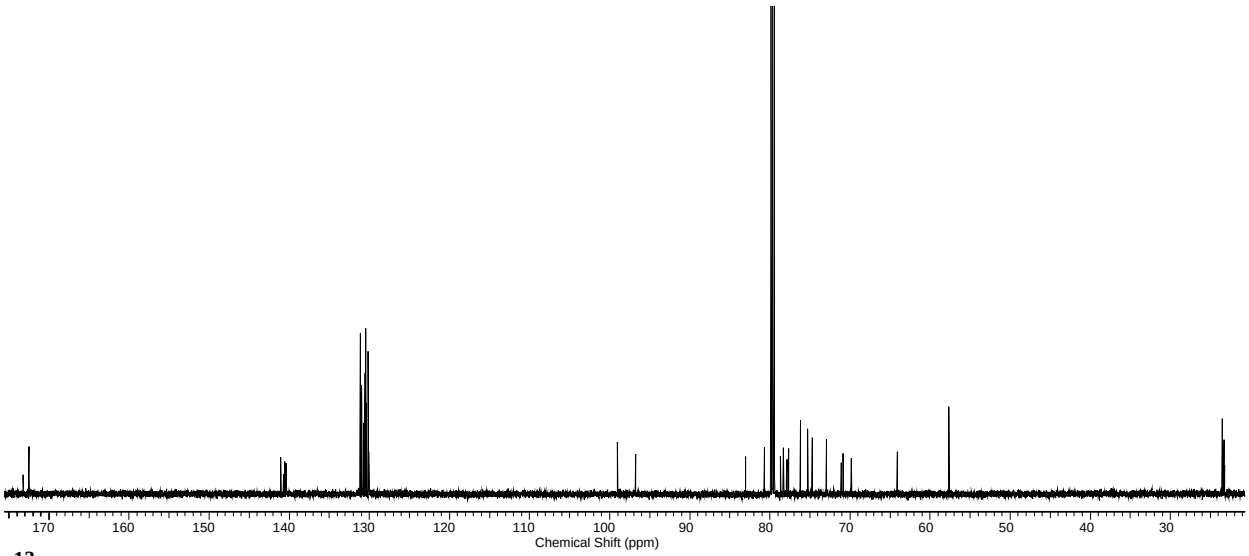
Methyl 2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (40)



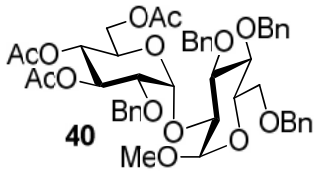
40



(^{1}H NMR 300 MHz, $CDCl_3$)



(^{13}C NMR 75 MHz, $CDCl_3$)



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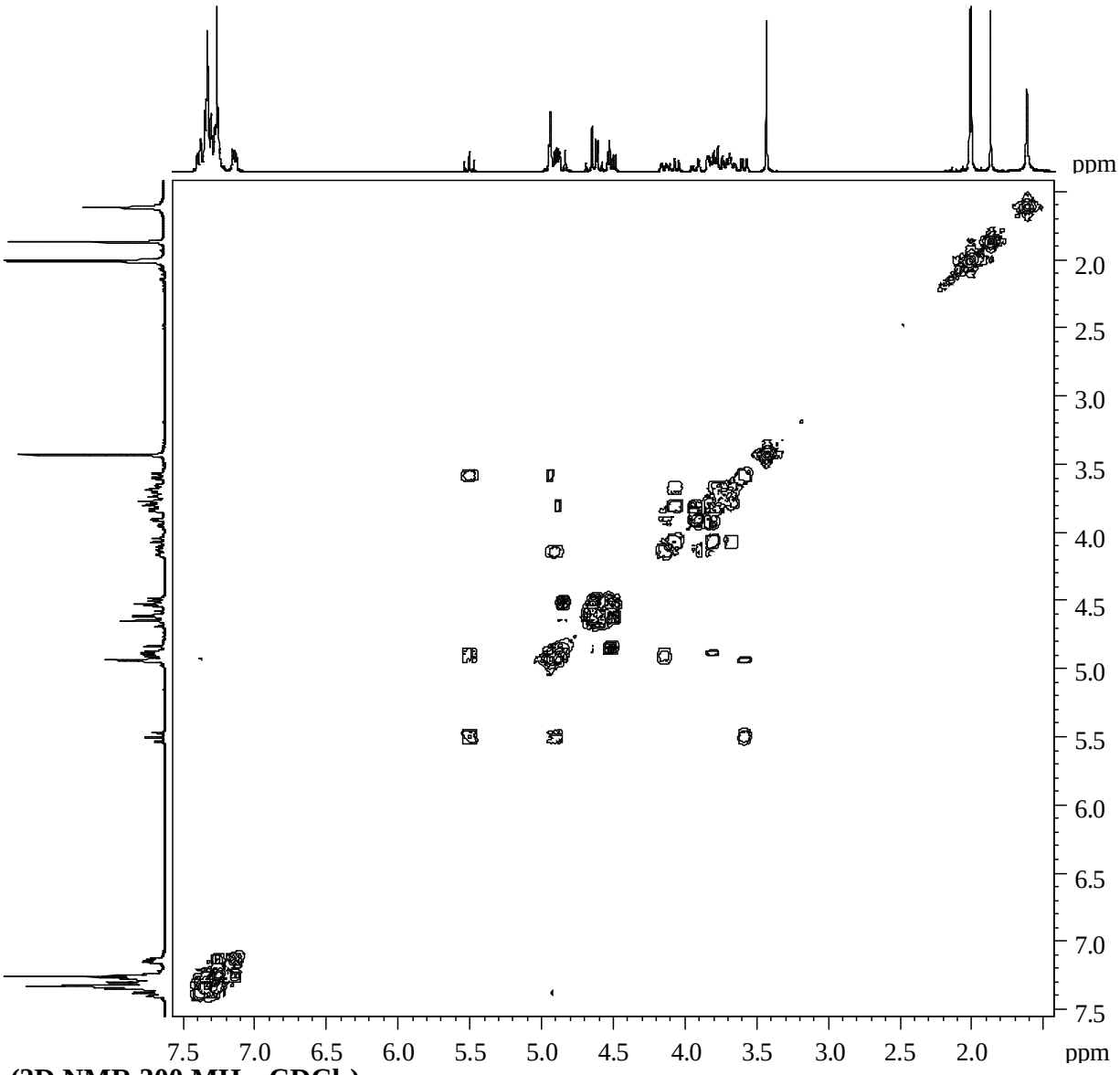

(2D NMR 300 MHz, $CDCl_3$)

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